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A
SYSTEM
OF
CHEMISTRY.

IN FOUR VOLUMES.

BY
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PREFACE.

No science has ever made a progress so rapid as Chemistry has done within the few years that have elapsed since the last publication of this work. Its general doctrines have been materially modified ; new views of theory have been introduced, having the most extensive relations ; substances before unknown have been discovered ; an immense accession of facts has been added ; the methods of analysis have been rendered more perfect, and principles applied which give greater precision to chemical investigations.

To give a just view of these important acquisitions, and to exhibit the science in its present state, have been my leading objects in preparing this edition for the press. At the same time it has been my wish to preserve the work within its original limits. And by condensing discussions which have no longer the same interest, or which the progress of discovery has rendered less necessary ; by abridging some details of inferior importance, or not strictly chemical ; and employing

rather a fuller page; I have been enabled to comprise all that has appeared to me essential without any material enlargement of size.

To the analytic method of arrangement, which I had adopted in the two preceding editions, I have still adhered, convinced that it is the one under which the just relations of the science are best exhibited free from hypothesis, and under which also a knowledge of its principles is most easily conveyed. But in some respects the order in the subordinate divisions has appeared to me to admit of alteration with advantage, more particularly in relation to certain theoretical views which have occurred to me. An explanation of these alterations will be found in the preliminary observations to the second volume.

For the introduction of the views to which I now allude, some apology may perhaps be required. One may be found in the unsettled state of chemical theory on the questions to which they refer. I could not avoid bringing them under discussion: And as I have elsewhere had occasion to remark, “in a science such as Chemistry, the principles of which do not rest on demonstration, but on probable evidence, it is of importance to present a subject in every light under which it admits of being surveyed.”

I have not ventured to make any change in nomenclature, but have usually employed the current terms, even where they are not altogether correct. The whole system has, by the progress of the science, been rendered defective ; but it would be premature to introduce at present any general change ; and this would be less excusable with the example so evident of the evils attending a theoretical nomenclature.

I have still made it a leading object to combine the advantages of a System for consultation with those of an Elementary Treatise. I have therefore continued, and rather augmented the marginal references. In a work in which it is necessary to limit the statements to the results of experiments, without including all the minute details connected with them, such references are important, as these details require often to be studied in new researches, or from their connection with particular objects ; and this can always be done most satisfactorily in consulting the original authorities.

EDINBURGH, NOV. 20. 1818.

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INTRODUCTION.

NATURE, OBJECTS, AND APPLICATIONS OF CHEMISTRY.—GENERAL VIEW OF ITS HISTORY.—
PRINCIPLES OF ARRANGEMENT.

THE external appearance of bodies leads in general to the conclusion, that they are homogeneous, or consist of matter essentially the same in each individual mass. In a portion of water, or in a fragment of marble, there appears to exist no difference of parts. A more minute examination discovers, however, that they are often composed of different substances, or of kinds of matter altogether distinct ; and these, by the operation of certain arrangements, are capable of being separated from each other, so as either to pass into new combinations, or to remain in an insulated form.

When different bodies are placed in contact or in mixture with each other, they often enter into intimate union, lose their individual existence, and form substances distinguished by the possession of new properties. And the composition of these substances can, by the operation of other forces, be again subverted, and the constituent elements restored to their original state.

Thus the varieties of matter pass through an extensive series of combinations and decompositions, occurring either in the operations of nature, and forming part of its established system, or effected by peculiar arrangements in the processes of art. From these arises the immense diversity of constitution and properties which the material world presents. The number of substances which can be ranked as simple is comparatively small. By mutual combination, numerous compounds are formed. These are farther capable of combining with each other, and of giving rise to more complicated products ; and thus, from a few elements, perhaps still unknown to us, an indefinite diversity of combinations is established. CHEMISTRY is the department of Science to which this class of actions belongs.

CHEMICAL ACTION is distinguished from other species of physical action by very appropriate characters.

First, It is exerted only between the minute particles of matter. When one body acts chemically on another, it is always from the particles of the one to those of the other that the action is exerted : the effect is therefore the subversion of the mass of each, and their transition into a new state, in which they are intimately blended. In other species of physical action there is no such result. One mass of matter acts upon another, modifying its motion, or its external condition ; but each with regard to its insulated existence remains unchanged.

Secondly, Chemical action is exerted at no sensible distance : bodies that act on each other chemically with the greatest force, suffer no change when placed at the smallest apparent distance : they require to be brought into contact, and even frequently into intimate mixture ; no sensible motion, therefore, of the particles between which it is exerted can be discovered, and it is inferred only from the change of constitution and properties which is the result. In the other departments of physical science, actions are investigated, which are exerted at apparent, and often at

immense distances : sensible motion is always the effect, and is sufficiently apparent to admit of determination with regard to its direction and force.

Lastly, Chemical action is productive of a change of properties in the bodies between which it is exerted. It unites their particles in new modes and arrangements, whence existing properties must be subverted, and others acquired; and it combines bodies, the properties of which opposing each other, must, to a certain extent, be modified by the combination. The result, therefore, is always some sensible alteration, and frequently the most entire change. Mechanical action is attended with no such effect. Its tendency is merely to communicate or modify motion in the masses on which it operates, and this can be productive of no change in their constitution or powers.

These distinctions are amply illustrated, in considering the points of view under which the same substance is regarded in a system of Mechanical and of Chemical Philosophy. In the former a Ray of Light is viewed simply as in motion; and the phenomena, which become the subject of inquiry, are those which arise from its transmission through bodies, its reflection from their surface, or its inflection towards them : in the latter its more intimate actions are traced, those in which it changes their properties or composition,—effects arising not from the motion of the entire ray, but from the repulsion the light communicates, or the combinations into which it enters. To the Mechanical Philosopher, Air is a subject of attention, as a mass possessing mobility, elasticity, and weight : the Chemist, on the other hand, submits it to experiment with the view of determining whether it is simple or compound ; he has succeeded in discovering its composition, and he traces the agencies of its principles in numerous chemical operations,—in exciting combustion, in promoting vegetation, and in sustaining animal life. Water holds a place in a system of Mechanical Science, merely as a fluid

acting by its impulse or gravity : while in Chemistry its combinations are investigated ; its elements are discovered ; and the operation of these elements, as they are disengaged in the decompositions it suffers, is traced, not only in numerous subordinate cases of chemical action, but on a scale of greater magnitude in some of the most important processes of nature. Lastly, Solid Substances are regarded by the Mechanical Philosopher only as they are endowed with figure, hardness, or cohesion, or as presented in various states of motion : from the Chemist they claim a more minute examination as to the actions which the particles of each exert towards those of others, and the combinations into which they enter. In all these cases, the investigations of the one department are directed to the sensible motions of masses of matter ; those of the other to the agencies of their minute particles, and the combinations into which these enter, producing not merely change of figure or of place, but changes of constitution and properties.

The powers from the operation of which chemical phenomena arise, are that species of Attraction which is exerted at insensible distances between the particles of matter, and certain forces of Repulsion by which it is modified. The mutual attraction exerted between particles of a similar nature unites them in masses, which derive, from the mode of aggregation, peculiarities of hardness and tenacity, of structure and form. Exerted between particles of different kinds, it unites them so as to form substances possessed of properties more or less different from those of the bodies of which they are composed. The power of Heat or caloric, establishing repulsion between the particles of matter, counteracts the operation of these attractions, and often modifies their results. Light, from its connection with heat, and perhaps also from its peculiar chemical agency, sometimes gives rise to similar effects. And Electric attraction and repulsion, under certain modifications, have an influence still more energetic in producing chemical decompo-

sition. Chemical changes depend on the operation of these powers in different degrees of intensity on the particles of bodies. And in conformity to these views, CHEMISTRY may be defined, the science which investigates the combinations of matter, and the laws of those general forces by which these combinations are established and subverted.

From the class of actions which it belongs to Chemistry to investigate, arise numerous applications to purposes of practical utility, or to the elucidation of natural phenomena ; an extensive series of changes which occur in nature being the results of chemical operations, and many of the arts consisting of a series of chemical processes. These applications, in all their extent, it would not be possible to trace within the limits of an introductory discourse ; but a general outline of them will convey some idea of the extent and importance of this science, and of the interest which its study is calculated to excite.

The ATMOSPHERE, or that mass of elastic fluid which surrounds the globe, is, by its chemical powers, an important agent in the production and regulation of natural changes. It serves, for example, to equalize the distribution of heat over the surface of the earth. Expanding, and becoming specifically lighter from increase of temperature, a current of air necessarily ascends from any part of the earth's surface that is much heated ; its place is supplied by colder air, which is pressed in from every side ; and the warmer air is wafted to colder regions, yielding in its progress the heat it had received. A circulation is thus established, by which the extremes of heat and cold, that would otherwise have rendered the greater part of the globe uninhabitable, are prevented ; while, by these motions of the mass of air, its purity is preserved. Nor does the atmosphere merely convey heat, and equalize its distribution ; it contains an immense quantity of the same power in a latent state, which, by various chemical combinations,

is rendered sensible,—which is the source of the heat produced by the burning of combustible matter, and of that which animals generate, preserving them constantly warmer than the surrounding medium. It is not less useful as the agent by which the circulation of Water is established. Assisted by heat, it elevates a portion of this fluid in vapour; which, condensed as the temperature falls, descends as dew, rain, or snow; and, by the declivity of the land, is conveyed over its surface, and returns to the ocean. Lastly, air is indispensable to the support of vegetables, and the existence of animals. To plants it affords a considerable part of their nourishment: to animals it is still more necessary, its abstraction for a few minutes causing death: and in both, its agency is chemical; it suffers changes of composition, and produces reciprocal changes in the animal and vegetable systems.

WATER is the medium of various important chemical changes in nature. Like air, it operates in equalizing temperature, partly by its motion, and partly by its changes of form; in passing to the state of ice it evolves heat, and absorbs it when it returns to that of water; and by both moderates the transition of seasons. It acts on the solid parts of the earth's surface, and causes their disintegration; and in supporting animals and vegetables, it undergoes decomposition, and furnishes principles which contribute to the formation of their products.

The operations of the MINERAL KINGDOM are more concealed from us: but we still perceive in their results the influence of chemical agency. The greater part of the substances which compose the crust of the earth are compounds, and have therefore been formed by chemical combinations; and the sublime, though obscure speculations of Geology, are founded on the conclusion, which facts establish, that attractions have at one time been exerted between these substances, or between their elements, while existing in the fluid form. Chemistry too affords the on-

ly sure basis on which the *species* of minerals are established and arranged, by determining the real composition on which alone their identity or dissimilarity can be determined.

Nor is chemical influence less conspicuous in the ANIMATED WORLD. The nutrition of animals and vegetables, and the formation of their various products, depend on new combinations of the elements of the substances they receive as food : these processes, though receiving some modifications from the circumstances under which they take place, are essentially chemical ; and chemistry is capable of elucidating some of the most important subjects of investigation in animal and vegetable physiology. In Vegetation we perceive a series of changes, the result in a great measure of chemical attractions. From the moment of its commencement, air and water are absorbed, are decomposed, and their principles combined in the vessels of the plant ; and from these combinations, the numerous and diversified products of vegetables are formed. If other agents are necessary, or subservient to the process, it is still by their chemical agency. Light, by the affinities it exerts, aids the decomposition of the water which the plant absorbs ; and manures accelerate the process, and improve its products, by furnishing, in a less combined state, and in larger quantity, the same principles which air and water supply. In the series of changes which are carried on in the Animal System, the influence of Chemistry is equally to be traced. In examining the process of digestion, it discovers the chemical quality of the gastric fluid, by which it is fitted to dissolve the food : in investigating the function of respiration, it unfolds the nature of the chemical changes which the blood suffers in the lungs ; the evolution of a principle, which, if retained, might prove hurtful, and the corresponding action of that part of the air which is necessary to life ; in the same process, it detects the source of animal heat, or of that power by which animals are enabled to preserve themselves at a tem-

perature superior to that of the medium around them: in perspiration, it discovers a function subservient to respiration, and fulfilling nearly the same purpose; and in secretion, it traces the various chemical products formed from a common fluid by the exertion of complicated affinities. Lastly, by analysing the fluids and solids of the animal body, it throws light on the researches of the Physiologist, and guides, even in some cases, the practical inquiries of the Physician.

The importance of Chemistry is not less conspicuous in its relation to the Arts. Strictly speaking, the origin of the greater number of the arts has been prior to the cultivation of any science; and their advancement has often depended on accident or on the mere routine of practice. Still, their principles are dependent on science; and a knowledge of these principles affords the most certain guide in attempting their improvement.

Agriculture, the most important of the arts, and that which is perhaps most susceptible of indefinite improvement, is more directly connected with Chemistry than with any other science. Vegetation, the regulation of which, so as to increase the products of useful plants, is the object of agriculture, is little else than a chemical process, or it consists of a series of changes of composition, terminating in the formation of new compounds. It must be admitted, that the causes by which these changes are effected are not wholly under our control. But neither are they altogether exempt from it. By certain arrangements of circumstances, hitherto, indeed, in a great measure empirical, we can accelerate the process, and even increase the quantity of product, or to a certain extent change its nature. Nor is it improbable, that, in these respects, our power may be farther extended, as our knowledge of the chemistry of vegetation is advanced. The influence of soil, and the action of manures, are already partly known; and there is no just reason to forbid the expectation, that

Chemistry may unfold more skilful modes of applying the agents on which the nutrition of vegetables depends, or of regulating those circumstances which influence the formation of their various products.

In the treatment of the products of vegetation, we often find chemical agency exemplified. In bleaching, by the application of a process purely chemical, we change the colouring matter of the thread, and render it capable of being easily removed. In dyeing, we extract the colours of many substances by solution, heighten their brilliancy by the admixture of chemical agents, and, by the intervention of others, fix and render them permanent in the cloth. In fermenting, by a proper regulation of circumstances, we change the principles of the fermenting substance, and form a very different product, wine, or fermented liquor : And, by distillation, we separate from this the ardent spirit, in which its principal qualities reside. The art of the chemist is not less strikingly displayed in the processes for extracting and refining sugar, preparing starch, indigo, and other substances ; in the fabrication of paper, and of many other useful products obtained from the vegetable kingdom. The principles of all these arts have been established by the researches of modern Chemistry ; and in the greater number of them, their manipulations have been improved by the application of scientific skill.

The adaptation of animal substances admits of similar applications. Tanning, the manufacture of soap, glue, and a number of others, are mere chemical processes, which Chemistry has successfully elucidated.

The mineral kingdom affords a number of substances, which, to be prepared for the uses to which they are applied, must undergo many operations of art ; and these are in general of a chemical nature. The extracting and working of metals, arts so important to civilized society, and the effects of which, in all their extent, it would be difficult to appreciate, are mere branches of practical che-

mistry. The production of glass, the most beautiful and one of the most useful gifts of art to man, is the result of a simple chemical combination. From variations in the process, and additions of certain ingredients, arise the arts of enamelling, and imitating the gems. And the processes employed in the fabrication of pottery and porcelain, depend on similar combinations, regulated entirely by this science.

Not only is Chemistry of advantage, from its relations to the arts; it is also interesting and valuable from the connexions it has with many of the practices of common life. Illustrations of this kind might be derived from the knowledge it conveys, by the discovery of the laws of heat. The peculiar effects arising from the action of this power on matter, the sensations it excites, its communication, and its evolution and absorption, constitute phenomena familiar in their occurrence, the scientific knowledge of which is in the highest degree interesting, and which admit of the most numerous and important applications. From the multiplicity of its objects, and the extent of its relations, there is no science indeed which can afford more interesting subjects of inquiry, which contributes more to enlarge our views of nature, or which promises more immediate practical utility. And there is none of which the progress in modern times has been so rapid, or in which the prospect of discovery is at present more unlimited. Its very nature leads to almost indefinite advancement; for on the one hand its object is to discover all the possible combinations of bodies, and on the other, by analysis, to discover their composition even to their ultimate elements; and these inquiries are so remote, and so extensive, that it is scarcely possible to fix any limits to which the progress of the science can be assigned.

Chemistry is a branch of knowledge which is peculiarly of modern origin. There are indeed traces from remote

antiquity of various arts, the principles of which are chemical. Metallurgy, or the art of extracting metals from their ores, of purifying, casting and forging them, must have been of early invention ; and the properties and uses of the more common metals were known at so remote a period, that we have no records of their discovery. Other chemical arts, as that of making bricks and earthen ware ; those of fermenting, bleaching, dyeing, and several others, were practised in the earliest ages. But there is no reason to believe that such arts were founded on any previous acquisition of chemical skill. They were the results of casual observations, or of experiments dictated by necessity, practised without the knowledge of any principle : and as a Science, or System of facts and reasonings, Chemistry was unknown.

Its claims to antiquity have not however been neglected by chemists. From the traces which can be discovered, at the most remote periods, of the practice of chemical arts, has been inferred the existence of chemical knowledge : almost every celebrated individual of early times has been revered as the inventor of some chemical process ; and many profound truths belonging to this science have been said, by those who advance these pretensions, to be concealed in allusions and allegories in the sacred writings and in the ancient mythology.

In Egypt, particularly, Chemistry is supposed to have been early cultivated. Thot, or Athotis, surnamed Hermes, by the Greeks, has been regarded as the founder of the science. The knowledge of it, which had nearly perished by some extraordinary revolution, was re-established, it is said, by Siphosas, the second Hermes, from whom Chemistry has been named the Hermetic Art. Its secrets, it is added, were deposited with the Egyptian priests, from whom the earlier Grecian philosophers acquired what chemical knowledge they possessed.

It is scarcely necessary to examine these pretensions.

The writings ascribed to Hermes are evidently spurious; the interpretations of the fables of antiquity, as unfolding chemical or alchemical processes, are fanciful and extravagant; and the rude practices of chemical arts afford no proof of the prior existence of the science to which they belong. These practices were doubtless altogether empirical; and in the chemical arts of the ancient nations, we do not discover a single trace of what can properly be regarded as a knowledge of any of the principles of Chemistry. The skill of the Egyptians in these arts has been highly celebrated; they worked mines of gold and silver; extracted other metals from their ores, and displayed dexterity in fabricating them for different purposes; they carried the manufacture of glass to considerable perfection, and knew the methods of colouring it, so as to imitate the gems: they discovered the processes for preparing sea-salt, alum, sal ammoniac, and mineral alkali, and applied these substances to various chemical uses: they were skilled in the arts of dyeing, embalming and making perfumes; they prepared various pigments, and introduced into their medical practice the products of rude chemical processes. Yet, with all this, they may have been wholly ignorant of Chemistry; and, accordingly, we cannot discover that these arts were practised with any knowledge of their principles, or were regarded as connected by any relations under one department of science.

Chemistry formed no part of the system of Grecian philosophy; for the speculations of the schools on the principles of bodies were altogether hypothetical, and had little or no relation to any chemical inquiry. And the observations respecting the chemical properties of bodies in the writings of Theophrastus, Aristotle, and others, are altogether vague and unconnected. The arts, under the progress of civilization and luxury, both among the Greeks and Romans, received some improvements. The pharmacy of the Greek physicians had become more complica-

ted, and contained a number of metallic preparations ; the art of tanning is of Greeian origin, as is also that of manufacturing steel : the Corinthians were skilled in making alloys, which imitated silver and gold ; and the statuaries excelled in the arts of purifying and casting the metals. But all these were practices isolated and empirical, widely remote from any application of systematic knowledge.

Can any cause be assigned for this slow progress of Chemistry ? While it remained nearly uncultivated, and even without a name, the foundations of other physical sciences had been established. Astronomy had been studied with success. Arithmetic and Geometry were early known : and these, with some other branches of physics, were advanced by the labours of the Greeian philosophers.

It may in part be ascribed to the peculiar nature of this science. Its most powerful agents, and those most extensive in their operation, are substances with which we are not familiar, and which are not easily recognised ; and the actions which it investigates being exerted between the minute particles of matter, are more obscure and complicated than those of the other departments of natural philosophy. The difficulty, therefore, of observing accurately the phenomena, and of discovering their causes, must have retarded the progress or rather the rise of the science. With this, another cause concurred. Chemical investigations can be prosecuted successfully only by experiment ; and this method of interrogating Nature, or at least its importance, was unknown in the ancient world. Arithmetic and geometry require for their cultivation only pure intellectual exertion ; and astronomy, as it existed among the ancients, depended for its advancement principally on observation. These sciences might, therefore, be successfully cultivated, while Chemistry, which is so immediately dependent on experiment, would remain unknown. The delusions of Alchemy gave rise to the experimental method of investigation, and thus not only laid the foun-

dation of chemical science, but perhaps contributed more than any other event to the superiority of the modern over the ancient method of philosophising.

To Alchemy,—the pretended art of converting the baser metals into silver and gold, a singular pursuit, which originated towards the decline of literature, and which continued for many centuries to be prosecuted with unabated ardour, Chemistry undoubtedly owes its origin. As a distinct branch of knowledge, it had no existence prior to the period when the researches of the alchemists commenced. The chemical properties of bodies had seldom been made the subject of investigation, and the slow improvement of the chemical arts was rather the result of chance, than of inquiries suggested by any principle. By the labours of the alchemists, some knowledge of these properties was attained, and gradually enlarged; their views led them to institute many experiments on the changes which bodies suffer from their mutual intimate actions, and these furnished the materials from which Chemistry was gradually raised. The knowledge thus slowly acquired, was indeed for a time directed to a chimerical object; but the value of the acquisition was not diminished, while the foundation was laid of more rational and successful investigations. “Alchemy,” says Lord Bacon quaintly, though with justness, “may be compared to the husbandman, of whom Æsop makes the fable, that when he died, told his sons that he had left unto them gold buried under ground in his vineyard; and they digged over all the ground, and gold they found none; but, by reason of their stirring and digging the mould about the roots of their vines, they had a great vintage the year following; so, assuredly, the search and stir to make gold hath brought to light a great number of good and fruitful inventions and experiments *.”

* Bacon's Works, 4to, vol. i, p. 18.

It is not possible now to discover from what circumstance this belief of the practicability of the transmutation of metals originated, nor how far it was connected with any previous acquisition of chemical knowledge. It is not easy even to ascertain the precise period at which it began to be entertained; for although the alchemists have endeavoured to prove the high antiquity of their art, their proofs rest on spurious writings, or forced and absurd interpretations of ancient mythology and history. No allusion to it is to be met with in the celebrated collection of Pliny,—a proof, that if it existed, it had attracted little notice in the first or second century of the Christian æra. Even prior to this period, however, it is supposed to have been cultivated in Egypt: an edict of Diocletian is quoted, in which, having suppressed a revolt of the Egyptians, “their ancient books which treated of the admirable art of making gold and silver,” are commanded to be sought out and committed to the flames; and this, Gibbon remarks, is the first authentic event in the history of Alchemy. It would be so were the reality of this edict established; but there is every reason to regard it as spurious, as the earliest author who mentions it is of the seventh century, and it is appealed to only by those who support the claims of the alchemists to the high antiquity of their art.

The word Alchemy first occurs in a work of Julius Firmicus Maternus, a writer said to be of the fourth century, and he mentions it as applied to a branch of knowledge then well known; but there are doubts whether the text is genuine. The art of transmutation is distinctly mentioned by a writer of the succeeding age, Æneas Gazeus: “those who are skilful,” he remarks, “can so change silver and lead, as to convert them into the finest gold;” but the authenticity of this passage is also not established. There are numerous writings ascribed to Greek Physicians and Ecclesiastics, said to be of the fourth, fifth, and sixth centuries, in which the art of ma-

king gold is the principal subject. The greater number of these remain in manuscript; many of them are evidently spurious; and it is doubtful how far any of them are of the age to which they have been assigned.

It appears, on the whole, however, that about the fifth century some progress had been made in chemical investigations, and Chemistry began to appear as a distinct branch of knowledge and a peculiar object of pursuit. This probably arose from the extension of the pharmacy of the Greek physicians, the processes of which had gradually become more complicated and more strictly chemical. It seems also to have in part originated from the metaphysical speculations of the schools on the transmutations of the elements of matter; its earliest votaries were of the sect of the New Platonics, and its study was associated with that of magic and of mystic theology.

If Alchemy originated in this period, it is among the Arabians, who had received the literature and science of the Greeks, that it was most eagerly prosecuted. Geber, who appears to have flourished about the commencement of the eighth century, and who is said to have been a Greek physician, though the epithet Arabian is usually attached to his name, may be considered as the first systematic chemical author. His work, which is professedly a compilation, describes the chemical processes then known; it contains a number of observations on the properties of several important chemical agents, belonging particularly to the classes of salts and metals; and delivers the theories, however vague and extravagant, which guided alchemical researches. It appears, that even at this early period, the dream of the universal remedy had been associated with the original object of the alchemists, at least this is the obvious interpretation of the following passage which Bergman quotes from Geber's works: "*Elixir rubeum omnes infirmitates chronicas, de quibus medici desperarunt, curat, et facit hominem juvenescere ut aquilam.*" Albucasis and

Rhazis, Arabian physicians, cultivated more particularly pharmaceutical chemistry. Avicenna is the author of that division of substances from their chemical relations into salts, earths, inflammables, and metals, which, with some modifications, has kept its place as the basis of almost every chemical classification even to the present times; and which, therefore, necessarily implies no inconsiderable advancement in the leading distinctions of the science.

When learning was transferred from the East to Europe, Alchemy was cultivated with increased ardour; and in the period extending from the 11th to the 16th century flourished the principal alchemists. Albertus Magnus, a Dominican friar of the 12th century, taught at Cologne, and appears to have been well acquainted with the metallurgic processes known at that time. Roger Bacon, a monk, a native of England, was nearly of the same period: he appears to have been master of all the natural knowledge of his age, and a number of curious chemical facts are to be found in his writings: he evidently alludes to phosphorus, a substance which has always attracted notice from its high inflammability; and he gives the composition of gunpowder, concealed in some measure under the form of an anagram. Arnoldus de Villa Nova, a French physician of the 13th century, has been distinguished as having introduced the application of chemistry to medicine; he is the first who mentions spirit of wine, and the pharmaceutical purposes to which it may be applied. His disciple, Raymond Lully, a native of Majorca, seems to have prosecuted his experimental researches; a number of chemical facts are to be found in his writings, and he is said to have been the first who proposed the chimera of the universal remedy. Isaac and John Isaac Hollandus, Dutch chemists, supposed to have been father and son, appear to have added to the prosecution of alchemical pursuits more valuable acquisitions in the chemical arts: they give a number of processes for the colouring of

glass, and imitating the gems; and the art of enamelling is considered as their invention. Basil Valentine, a German monk, extended the application of chemical remedies, and more particularly of the preparations of antimony to medicine; and he is noted among the alchemists as the author of the hypothesis of the three chemical elements of salt, sulphur, and mercury. Paracelsus, a native of Switzerland, of the 15th century, contributed perhaps more than any person of that age to the diffusion of Chemistry, by the enthusiastic zeal with which he brought forward the employment of chemical remedies, and with which, at the same time, he attacked the Galenical doctrines of the schools. His disciple, Van Helmont, followed the footsteps of his master, with rather more sobriety, and conferred real benefit on Chemistry by some of his observations and experimental researches, those more particularly on the elastic fluids disengaged in many chemical operations,—an important subject, to which he first attracted the attention of chemists.

In these successive labours, too, a number of discoveries, not easily appropriated to their respective authors, had been made. The principal mineral acids, which were unknown to the ancients, the sulphuric, nitric, and muriatic, had become known to the alchemists; as had also the nitro-muriatic acid, and its property of dissolving gold. The three alkalis, under forms more or less pure, had been discovered, and processes given for their preparation. A number of the neutral salts were clearly distinguished; borax is mentioned even by Geber. The metallic salts having been still more the objects of experiment, many of their properties were observed, and processes for preparing them described. And the number of the metals was augmented by the discovery of zinc, antimony, bismuth and arsenic.

Chemistry, therefore, at the conclusion of this period, though obscured by the follies of Alchemy, had become

rich in facts and experiments ; some of its most powerful agents had been detected ; the instruments of its principal operations invented, and the methods of conducting its processes improved ; the chemical arts had advanced to greater perfection ; and the principles of the science were even so far developed, that the absurdities by which its progress had been retarded began to be perceived, more rational objects of investigation engaged the attention of its cultivators, and more correct views of theory guided their researches. The application, too, of chemical preparations as remedies, connected Chemistry with Pharmacy and with the more liberal profession of Medicine ; and the attention of those who prosecuted these researches was thus withdrawn from the fruitless pursuit after the art of transmutation, and directed to an object beneficial in itself, and unconnected with concealment and imposture.

The general revolution in Philosophy which overturned the scholastic system, and established the method of induction from observation and experiment, contributed to the improvement of Chemistry in common with the other physical sciences. Bacon first assigned it its proper rank in the scale of natural knowledge, and, in his masterly survey of human knowledge, pointed out its peculiar characters ; he reviewed its history ; investigated the causes which had obstructed its advancement, and suggested a number of investigations which he supposed might be successfully prosecuted. Chemical inquiries formed a principal object of attention among the learned societies instituted for experimental investigation ; and these inquiries soon assumed that form, and were conducted with those views, which continued afterwards to mark the progress of natural philosophy in all its branches.

In these labours, Kunckel, Homberg, the two Lemerys, and the Geoffroys distinguished themselves. In England, Boyle, Hooke, and Mayow were occupied principally in researches on the aërial fluids disengaged in chemical

operations, and on the influence of atmospheric air in combustion and in respiration. They shewed the extrication of aërial matter in numerous cases of chemical action, and observed the difference of these airs and vapours from atmospheric air. They also proved that the presence of the air is necessary to support combustion, and that in sustaining this process it suffers diminution of volume. The state of knowledge, however, was not sufficiently advanced to admit of those investigations being followed with success; and though they led to some anticipations of important truths established at a later period, they were not immediately prosecuted, their importance was not duly appreciated, and they had little influence in the progress of the science.

Chemistry is indebted to Newton for the generalization of its phenomena, so far as relates to the peculiar power on which they principally depend. Having demonstrated the laws of gravity, and their application to the sensible motions of the universe, his views suggested the speculation which had before been but hinted at, that there might exist other species of attraction, exerted not at measurable distances, but only between the minute particles of matter in apparent contact; and that to such an attraction the phenomena of chemical action might be ascribed. He reviewed, in conformity to this supposition, the principal facts in Chemistry known at that period; from these he inferred the existence of this attraction, and from its exertion among bodies with different degrees of force, explained the phenomena of combination and decomposition. These conclusions were soon adopted by chemists. Stahl illustrated them, and Geoffroy attempted to investigate the relative forces of attraction among bodies, and exhibited them in the form of tables,—a happy contrivance, which contributed to give more precision to chemical reasoning. Boerhaave presented the general doctrines and the processes of chemistry in a systematic form, and with much

just criticism on the absurdities by which its progress had been retarded. Hoffman, his cotemporary, and his rival as a systematic physician, contributed in a similar manner, as well as by some experimental researches, to the advancement of the science. And Neuman, Pott, Brandt and others, in the same spirit of just investigation, prosecuted a number of researches, which the existing state of knowledge suggested.

Hitherto, Chemistry might be considered as nearly a collection of insulated facts, no general theory of the elements of bodies and their mutual actions and combinations having been framed. This had indeed sometimes been a subject of speculation in the schools; but in a manner altogether vague and hypothetical, and having no relation to chemical investigation. The chemists, perceiving the importance of their researches in leading to a knowledge of the constitution of bodies, began to advance different views; the chemical agents which they had discovered to be most general and powerful in their action, they naturally considered as the elements of matter; and hence arose their speculations with regard to salt, sulphur and mercury, water and earth, as elementary principles. Beccher, a German chemist, endeavoured to mature and refine this system; and his views excite interest, as having given rise to the celebrated hypothesis of his countryman Stahl.

Beccher had advanced the notion, that the properties of combustile bodies, and particularly their inflammability, depend on a common principle, Inflammable earth, as he named it; and fire or burning he considered as the effect of this principle brought into motion. Stahl so far adopted these ideas, as to suppose the existence of a common principle of inflammability; but he regarded it simply as the matter of heat and light. He gave it the name of Phlogiston, or Pure Fire. Combustion he considered as the evolution of this principle, whence the production

of light and heat which attend it; the substance which remains after the combustion he supposed to be the base with which the phlogiston had been combined: having lost this principle, it is of course no longer inflammable; but if it receive it from another inflammable substance, the former regains inflammability, which the latter loses. Stahl extended these views to the other cases of chemical action, in which changes are produced analogous to those of combustion, and thus formed a system which was extensively connected with the details of the science. Though no proof was given of its truth, it appeared to afford a satisfactory explanation of the more familiar phenomena of combustion; and it connected a number of analogous facts. For a considerable period, therefore, it was universally received; and the implicit faith which was given to it conveys an useful lesson with regard to the caution with which a theoretical system ought to be received. It continued to be defended long after its imperfections had become apparent; and was even relinquished with reluctance after it had been proved to be founded on an imperfect knowledge of the changes which take place in combustion, and to involve assumptions altogether false.

At this period the history of Chemistry as a science may properly be said to commence. The methods of strict analysis were first employed by Margraaf, and were soon afterwards improved by Bergman, by whom also was introduced that precision in assigning the proportions of the elements of compounds, and in general, indeed, in conducting chemical researches, so indispensable to their value. The same chemist ably illustrated the doctrines of attraction. Rouelle, Macquer, Cronstedt, Gahn, and others, enriched the science by numerous researches in its different departments, elucidated its principles, reformed its processes, and extended its limits by the analysis of compounds, and by the discovery of simple substances, which had not before been distinguished.

Another aera commences with the researches of Black. The disengagement of elastic fluids in chemical experiments had often been observed ; some facts were even known with regard to their more obvious properties ; and the experiments of Boyle, Mayow and Hooke, on the influence of atmospherie air in the processes of combustion and respiration, had they been well understood, established important results. But the state of knowledge in this department of Chemistry was extremely imperfect and vague ; and the first precise ideas with regard to the chemical agencies of these aërial substances were communicated by Dr Black's discoveries. In examining the properties of an earthy body, magnesia, then newly discovered, he found reason to conclude, that in certain states it contains a portion of an aërial substance, from which in others it is free. The same result he established with regard to lime, and the alkalis ; and though he did not actually obtain this substance, Fixed Air as he named it, he clearly demonstrated its existence, shewed that it is subject to the laws of chemical attraction, and that it produces important modifications in the properties of the bodies with which it combines. His still more profound discovery of Latent Heat, threw light on the formation of aërial substances, and on the most striking phenomena which attend their combinations.

These discoveries opened a path of investigation, the prosecution of which ultimately led to those views which gave rise to what has been named the Modern Theory of Chemistry. Cavendish procured the fixed air of Dr Black in its insulated form, and ascertained its most striking properties. He discovered another aërial body altogether different in its nature, distinguished by its great levity and high inflammability. And at a later period, Chemistry was indebted to him for the brilliant discoveries of the composition of water, and of nitric acid. Priestley prosecuted these researches with still more ardour, and in the career

of Pneumatic Chemistry surpassed all his cotemporaries in the number of his discoveries. Those of greatest importance are the knowledge of oxygen gas, and of its power of supporting combustion and animal life by respiration, of nitrous and nitric oxide gases, of ammonia, of muriatic, fluoric, and sulphurous acid gases, and the effects of vegetation on atmospheric air; to which are to be added numerous insulated facts of minor importance, many disquisitions on questions connected with chemical theory, and the invention of the most useful instruments and methods of operating on the gases. To Scheele, a Swedish chemist, is likewise due the discovery of oxygen, Priestley's investigations with regard to it being unknown to him. He farther demonstrated its existence as an ingredient of atmospheric air; detected the distinctive properties of nitrogen, the other elastic fluid with which it is combined, and thus established the grand discovery of the composition of the atmosphere. In other departments of Chemistry his acquisitions were numerous and important; and to Scheele, above all chemists, is due the praise of having accomplished, under the fewest external advantages, and with means comparatively inadequate, the most splendid discoveries, difficult in themselves, requiring the most accurate discrimination, and the highest exertion of inventive skill; and some of them such, that so far from being the results of the progress of the science, they might but for his labours have remained still unknown.

Lavoisier had also entered the path of Pneumatic Chemistry, and to him belongs the merit of discovering more clearly the relations unfolded by the modern researches, and the views to which they led. The hypothesis of Stahl was at this period universally received by chemists, and the numerous facts recently established were endeavoured to be reconciled to it, even when they appeared most adverse to its principles. Lavoisier detected its fallacy; perceived that it was founded on an imperfect knowledge of the pheno-

mena it attempted to explain ; and that it was subverted by the progress of the science. The influence of the air in combustion had not altogether escaped observation : it had even been demonstrated by the experiments of Boyle, Mayow, and Hooke, that its presence is indispensable to burning. But this had passed unnoticed by Stahl. It had now been placed in a clearer light, and established with more precision. In particular, it had been shewn, that the power of atmospheric air in supporting combustion depends on its oxygen, which is uniformly consumed during the burning. Various hypotheses were framed to reconcile these facts with the doctrine of a common principle of inflammability. Lavoisier, finding no just proof of the existence of such a principle, was led to reject it, and drew the simple conclusion, that the oxygen of the air which disappears in combustion combines with the combustible body. Availing himself of Dr Black's discovery, that bodies in the aëriform state contain a large quantity of heat, not sensible by its usual effects, he ascribed the elevation of temperature, which attends combustion, to the evolution of this heat in consequence of the oxygen losing its aërial form. The phenomena of deflagration and detonation, and the calcination of metals, were explained on the same principles. The substances formed by combustion being in a number of cases possessed of the properties of acids, the same views led to the theory of acidity ;—that this general chemical property depends on the action of oxygen,—and on the same fact of the presence of oxygen in acids, their chemical agencies were explained. A system was thus formed, which embraced an immense number of chemical phenomena, and was indeed more or less strictly connected with nearly all the departments of the science.

This system, though superior to the established doctrine in simplicity, in the evidence of its principles, and in their adaptation to the phenomena, was received with

reluctance : it was at first indeed warmly opposed by nearly all Lavoisier's cotemporaries, and continued for a time to be rejected by those of the highest eminence. Supported, however, on its real merits, defended by just reasoning, and confirmed by experiments distinguished by their precision, it was finally established. In France La Place, Berthollet, Guyton, and other chemists of celebrity, united in its defence. In other countries it gradually gained strength. And although the progress of discovery has led to some modification of its principles, there remains to it the high distinction of an induction which overturned a false hypothesis, which constituted an important stage in the advancement of the science, which in many of its parts is just, and which will always form a leading division of chemical theory.

Subsequent to this period, Chemistry continued to be enriched with numerous insulated discoveries : the doctrines of heat had been more minutely investigated by Irvine and Crawford : those of attraction were prosecuted by Kirwan, Richter and Berthollet ; new substances were discovered, and their chemical relations traced, and more accuracy was given to the results of former investigations. At no distant interval, the discovery of Voltaic Electricity added another department to the science ; and the pile of Volta conferred a powerful instrument of analysis, the application of which led to the knowledge of the constitution of some important compounds. Still more recently, the discovery of certain laws which regulate chemical combination has brought calculation to the aid of experiment, and may ultimately give to the researches of Chemistry some degree of mathematical precision. While by these and other discoveries, the aspect of the science has, within these few years, been materially changed, much of what was regarded as established has been rendered doubtful, and new views of theory have been introduced, which remain at present the subjects of discussion.

The last object in this introductory discourse is to state the principles on which the objects of Chemistry are to be arranged.

The series of physical actions to which its investigations are directed, arise from the operation of certain general forces on the particles of matter, producing changes in the mode of existence, in the constitution, and properties of bodies. The science, therefore, obviously divides itself into two great departments; the first comprising the investigation of the general effects and laws of these forces, the second referring to their operation on individual substances. Under the former are placed the doctrines of Attraction, and of Repulsion as produced by the operation of Heat, Light and Electricity: To the latter belongs the history of the chemical constitution, properties, and combinations of all known bodies.

There is little difficulty in determining the order in which these divisions ought to be arranged. Without some previous knowledge of the general principles of Chemistry, it is impossible to state its particular details with advantage, while such a knowledge facilitates at once the acquisition and arrangement of its individual facts and applications. The objection has been urged indeed, that it is from these facts that the principles are inferred, and that the latter, therefore, cannot be illustrated while the former remain unknown. But this difficulty is one unavoidable, to a certain extent, in either mode of arrangement. In comparing it in relation to each, with the corresponding advantages, it appears to me that the first method is entitled to decided preference. It is possible to illustrate the general laws of chemical action by examples from substances familiarly known, or which, though unknown, are equally adapted to convey illustrations of abstract truths; and these laws being established, the details of the science can be stated with more precision, and rendered more interesting, than when its insulated facts are

presented unassisted by any knowledge of the principles which unfold their relations.

The arrangement in the first division admits of little diversity. The most natural order is that of placing first the doctrines of attraction, and after these, the consideration of its antagonist powers. The second division involves greater difficulties. The subjects belonging to it are extensive and complicated, and admit of being associated under very different chemical relations. Hence the numerous systems of classification under which individual bodies regarded as objects of Chemistry have been classed. A view of the arrangement I adopt is prefixed to this division, at the beginning of the second volume. The first division forms the subject of the present volume.

SYSTEM OF CHEMISTRY.

PART I.

OF THE GENERAL FORCES PRODUCTIVE OF CHEMICAL PHENOMENA.

ALL the phenomena of Chemistry arise from the attractions and repulsions which are exerted between the particles of matter. By attraction these particles are combined together; and did no other force operate, a state of equilibrium would be established, and matter, so far as relates to any change of constitution in bodies, would become quiescent. This is counteracted by certain powers of repulsion; and by the varied operation of these general forces, that succession of chemical changes which forms part of the economy of nature, and all those chemical processes which are effected by artificial arrangements, are called into action and sustained. The statement of the effects arising from the action of these forces, and the investigation of the laws they observe, are included under what may be regarded as the general principles of the science. According to the plan I have adopted the doctrines of ATTRACTION are first to be considered.

BOOK I.

OF ATTRACTION.

THE term Attraction is employed to denote that power or force by which bodies have a tendency to approach to each other, to enter into more or less intimate contact or union, and to remain in that state. Different varieties of attraction have been distinguished, which, whether they be ultimately the same or not, give rise to different phenomena, and operate according to different laws.

A general distinction may be stated between them, as they operate at greater or at less distances, and as they affect the masses or the particles of matter.

Gravitation, the most general in its agency of any of these attractive powers, is exerted between the largest masses of matter, at sensible, and often at immense distances; its tendency is to cause them to approach until their surfaces are in contact; its force, according to the law demonstrated by Newton, being directly as the mass or quantity of matter, and inversely as the square of the distance. The Magnetic and Electric Attractions, though they act only on certain bodies, or under peculiar circumstances, so far coincide with the attraction of gravity, as to operate at sensible distances, and on masses of matter, and even, as some have attempted to prove, according to the same law.

There are other varieties of attraction, which do not affect masses of matter, but are exerted only between its minute particles, and which operate at no sensible distances, but only at apparent contact.

Of this, Contiguous Attraction as it may be named, two varieties have been distinguished; one the Attraction of Cohesion or Aggregation; the other, Chemical Attraction or Affinity. The former is exerted between the particles of the *same* kind of matter: it unites them so as to form a mass or aggregate, the density or solidity of which is proportional to the force with which it is exerted, but the essential properties are the same with those of the particles which compose it. The latter is exerted between the particles of *different* kinds of matter; and when it unites them, forms substances having qualities which differ more or less from those of the bodies which have been combined.

The question has often been proposed, whether these attractions may not depend on one general cause, modified in the varieties under which it appears by external circumstances, or whether they are originally distinct from each other.

It is no doubt true, that distant and contiguous attractions observe different laws; or rather it cannot be shewn from any phenomena, that in contiguous attraction between the particles of matter, the law exists, which governs distant attraction between its masses. The idea has been conceived, however, that any difference which exists may depend on the modification arising from figure. Buffon remarked, that on the attraction of large bodies, placed at vast distances, the figures of the masses can have no perceptible influence; while in contiguous attraction, exerted at insensible distances, the figure of the particles, as altering the relative distance, must necessarily operate. Bergman adopted this view, and Macquer added to its probability, by the observation, “ that if gravitation be an essential property of matter, as there is reason to believe, its effects

cannot be confined to very large bodies, separated by immense distances, but must likewise act between their minute particles at small distances, and consequently be concerned in chemical phenomena."

It must be admitted, however, that no case of contiguous attraction has been demonstrated from the general law of gravity, modified by any assumption with regard to figure; and these speculations, whatever probability they may have, are not sufficiently precise to serve as the basis of any theory. And as we are unable to ascertain the figures and positions of the particles of matter, the laws of contiguous attraction cannot be deduced *a priori*, but must be inferred from the observation of its effects.

There is less reason to doubt but that the two varieties of contiguous attraction, aggregation and chemical attraction, are ultimately the same power, the different effects produced by their action arising from the difference in the particles they unite. In the one case, the particles being of the same kind, must form an aggregate possessed of their general properties; in the other, the particles being dissimilar, must, by their union, have their properties more or less changed. Admitting their identity, however, the effects they produce are so different, that they require to be considered apart.

CHAP. I.

OF THE ATTRACTION OF AGGREGATION OR COHESION.

AGGREGATION, or that attraction exerted between particles of the same kind of matter, is a force which often operates in chemical phenomena, modifying the exertion of chemical attraction, and counteracting the action of heat. Hence its effects are subjects of chemical investigation.

The existence of this attraction is easily demonstrated. If two particles of a similar kind, sufficiently fluid to be susceptible of motion, are made to approach, they unite when they are within a certain distance of each other; and the attraction by which this is effected retains them united, or opposes resistance to any force, the tendency of which is to occasion their separation.

In a solid mass of matter this power acts with the greatest force. The particles which compose the mass are united by a reciprocal attraction, of such strength that they are not capable of being moved, with regard to each other, by any mechanical agent; and considerable resistance is opposed to their disunion. In different solids it is exerted with different degrees of strength. In liquids it appears to be much weaker, or at least it is exerted under such a modification that a slight impulse is sufficient to disunite the parts, and scarcely any resistance is opposed to any force, the operation of which is to bring these into new arrangements. Lastly, in substances existing in the state of vapour or of air, it is entirely overcome. The particles,

instead of attracting, repel each other; they are made to approximate only by pressure, and they recede when this is withdrawn. Bodies exist, therefore, in the aëriform, the liquid, or the solid state, according as this attraction is exerted between their particles; and it is this power which unites their particles.

Aggregation is weakened or overcome by two causes, —by the operation of heat, or by the attraction which may be exerted by the particles of one body to those of another.

If a solid substance is exposed to heat, its volume is enlarged; the particles composing it, therefore, are separated from each other, and the attraction by which they were kept in union is counteracted. The enlargement of volume continues to proceed, as the heat is increased, until the point is reached at which the attraction is so far modified that the body passes into the fluid form. If the application of heat be continued, the particles are still farther separated from each other; and this continues increasing, until the attraction between them is overcome, a repulsion is established, and the fluid passes into the aërial form.

The same changes may be produced by the exertion of chemical attraction. If a liquid be poured on a solid, it often happens, that from the mutual attraction exerted between them, the aggregation of the solid is subverted, its particles are detached, and diffused through the liquid, so as to be no longer perceptible, and not even to impair the transparency. This constitutes the chemical process named Solution, which is merely a case of chemical combination, differing from others in the circumstance that one of the bodies exists in the liquid form, and communicates that form to the other. It is the result of the predominance of the mutual affinity of the liquid and solid over the cohesion of the solid. The affinity exerted to a solid by a substance in the aërial form, may in like man-

ner overcome its cohesion, and cause it to pass into the aëriform state. And even the mutual attraction exerted between two solids is sometimes such, as to diminish the power of cohesion in each so as to admit of their union, and their transition to a liquid state. Heat, by diminishing cohesion, promotes these changes.

When these powers, whether of heat or chemical affinity, are withdrawn, cohesion resumes its force. By reducing heat sufficiently, an aërial body may be brought to the state of fluidity ; and liquids, by sufficient cooling, may be rendered solid. The suspension of chemical affinity, in other cases, gives rise to the same changes of form, so that a solid is deposited from a liquid, or air, in which it had been dissolved.

When the attraction of aggregation is thus exerted, the particles are sometimes united indiscriminately, so as to form irregular masses ; sometimes they pass into arrangements, whence masses of regular figures arise.

The former happens generally when attraction is exerted suddenly, and with considerable force. If a liquid be suddenly cooled to a sufficient extent, a mass is formed altogether irregular. Or if a substance be produced by chemical action, the particles of which have a strong mutual attraction, this is exerted at the moment of its production, and it is separated in the form of a powder. This latter case is named in chemical language Precipitation, and the substance is said to be precipitated.

The other result occurs, when aggregation, previously weakened, either by the operation of heat or of chemical attraction, resumes its force more slowly ; the particles then assume a particular arrangement, so as to form masses of regular figures, or bounded by plane surfaces and determinate angles. This result is named Crystallization, and such regular figured masses are denominated Crystals. As a chemical operation of considerable importance, it requires to be more fully considered.

Crystallization is of two kinds : first, as it takes place by cooling from fluidity produced by heat, and secondly from fluidity communicated by the operation of a solvent.

Of the first kind of crystallization, water affords an example, in passing into ice. Long slender spiculæ form in the fluid, and from these others shoot out at a certain angle, and this continues till the interstices are filled with these crystals, and the whole becomes a solid transparent mass. We have also examples of it in the metals, and many other substances which, when melted and cooled slowly, assume symmetrical forms.

Of the second kind of crystallization, the principal examples are derived from the order of salts, and a few other solids soluble in water ; and with regard to this, several facts of importance require to be stated.

The solution of a solid in a fluid being increased by heat, a larger quantity of the solid is kept in solution at a high than at a low temperature. If we prepare, therefore, a solution of a salt in hot water, so that the fluid has dissolved as much of the salt as it can do, on allowing it to cool, the additional portion of salt which the heat enabled the water to dissolve, separates, and unless the cooling is very rapid, the particles of the solid, in approaching to each other, pass into those regular arrangements which constitute crystals.

The same result is obtained by withdrawing part of the liquid by which the solid is dissolved. If this be done slowly, as by spontaneous evaporation, the particles obey the law of attraction which unites them in regular forms ; and crystals are in this way formed, frequently more regular, and of a larger size, than by reducing the temperature of the solution.

In both cases, the fluid in which the crystals form is still a saturated solution of the solid, and on a farther evaporation, affords crystals.

The slower the formation of a crystal, the more perfect

is its symmetrical arrangement ; it is also larger, harder, and more transparent : while, when the process is rapid, or is disturbed by agitation, the arrangement is less regular, and the form incomplete. Hence the crystals formed in nature are in general more perfect than those produced by artificial processes.

Crystallization is promoted by affording a nucleus or solid point at which it may commence, and still more so if a crystal be introduced into the solution. Crystallization immediately commences from it, if the solution be a saturated one, and it is even capable of causing a part of the solid to be separated which the water at the temperature at which it takes place could have retained dissolved. Even the regularity of the figure of the crystal has an effect in rendering the crystallization more regular ; and on this Le Blanc gave a method of obtaining large and perfect crystals. It consists in selecting very regular crystals of a salt that have been newly formed, and putting them into a saturated solution of the same salt. They increase in size ; and as the side which is in contact with the vessel receives no increase, they are turned daily, to preserve their regularity. After some time, the largest and most regular of these crystals are selected, and the same process is repeated on them *.

The access of the air has an important influence on this process. If a saturated solution of salt, while hot, be put into a vessel from which the air is excluded, it does not crystallize even when cold. But when the air is admitted, the crystallization instantly commences, and proceeds with rapidity. This effect was supposed to depend on the pressure of the atmosphere, which, when suddenly introduced, causes approximation of the particles of salt in the solution, and thus favours the exertion of their mutual attraction, so as to cause crystallization. And in support of this

* Journal de Physique, tom. lv, p. 300.

it was stated by Dr Higgins, that any pressure, equivalent to that of the atmosphere, as the pressure of a column of mercury, has the same effect *. This explanation, however, does not appear to be altogether just. Some anomalous facts have long been known with regard to the experiment, particularly that the result, even with solutions of the same strength, is uncertain; the salt sometimes crystallizes in part, even while the air is excluded: sometimes, on the other hand, the crystallization does not take place when the air is admitted, unless agitation be employed; and sometimes not even with the aid of this, unless a crystal of the salt be dropt in, which acting as a nucleus always causes it to commence. It occurs only with regard to some salts, more particularly with sulphate of soda; while there are others, as nitre, alum, sulphate of potash, muriate of ammonia, and phosphate of soda, which crystallize from their saturated solution with equal facility in vacuo as under exposure to the atmosphere. Gay-Lussac farther found, that if the air be excluded, though the pressure of the atmosphere be admitted, as by the simple contrivance of putting a layer of oil over the solution while hot, crystallization does not take place when the liquor is cold, but it instantaneously happens when a crystal of the salt is dropt in: he also found, that the crystallization was not produced, when the air was excluded, by the pressure of a column of mercury being applied; while, on the other hand, when the solution remains in vacuo under diminished pressure without crystallizing, the introduction of the smallest quantity of any aëriform fluid causes it to crystallize †. Some similar results were observed by Dr Cox‡. These facts seem to prove, that the effect of the air does not depend on its pressure. Gay-Lussac supposed that its action might perhaps depend

* Minutes of a Society for Philosophical Experiments, p. 89.

† Philosophical Magazine, vol. 44. p. 44.

‡ Annals of Philosophy, vol. 6. p. 101.

on the circumstance of the air of the aqueous solution being expelled during the boiling, and hence of a portion of it being absorbed on its admission, which lessening the solvent power causes the precipitation of the salt. Yet he remarks, as unfavourable to this supposition, that a very small quantity of air is absorbed by a saline liquor, and even this takes place very slowly. And the fact stated by Dr Coxe, of the saline liquor remaining exposed to the air without crystallizing until agitation be employed, does not accord with this opinion. The effect, after all, probably depends principally on the agitation changing the position of the particles, and the percussion causing their approximation. The effect of agitation is undoubted. If the pressure of the atmosphere, or any equivalent pressure, be slowly and equably applied, it will act on the whole mass of fluid, and hence the effect may not be obtained. But if pressure be introduced suddenly, the agitation and the percussion at the surface may cause the approximation of the particles and their change of position, and hence the effect obtained by Dr Higgins in this mode. And even the sudden introduction of a portion of air without much pressure, may by the agitation produce the effect. The crystallization of some salts may depend more than that of others on certain positions of their particles, perhaps from their figure or magnitude; and this may be the reason why they are differently affected by these causes, with regard to the facility of the result.

During crystallization heat is rendered sensible: this is apparent in the experiment just stated, from the rapidity of the crystallization. In many cases, the volume of the substance crystallizing is enlarged, as in the examples of water, iron, and a number of salts; in others the volume is diminished. Quicksilver, in congealing, contracts about $\frac{1}{23}$ of its whole bulk; yet it exhibits the crystalline texture, and when the congelation is partial, the crystalline figure can even be discovered.

Crystals deposited from water always contain a quantity of it, which is retained by the affinity of the solid, and has passed with it into the concrete form. It is termed Water of Crystallization. Its quantity is various; sometimes it equals or exceeds the weight of the solid, and sometimes it amounts only to a few parts in the hundred. If the water of crystallization be expelled from a crystal, it loses its transparency and density, and at length its form. Crystals when they part with their water of crystallization on exposure to the atmosphere, are said to *effloresce*, and to *deliquesce* when they attract water and become humid. These results, however, depend much on the state of the atmosphere with regard to humidity. In a very dry atmosphere almost all salts are efflorescent, while in a humid atmosphere they are usually more or less deliquescent, and some of them considerably so, which in a drier air suffer no sensible change.

Besides the portion of water existing in combination with the salt, as water of crystallization, a portion may, and frequently is lodged mechanically diffused in the crystals. Berzelius remarks, that crystals are not perfectly solid, but rather consist of laminae united together; and in the interstices of these, a portion of the liquor from which the crystals have been formed may be retained. Hence the reason that the crystals of salt, which have been formed from a solution containing also other salts, is almost uniformly impure, from a slight intermixture of them; and are only purified by repeated crystallization, by which the quantity of this becomes at length imperceptible; and hence also he affirms, that crystals of a small size are purer than those which are large. It is this water, and not the proper water of crystallization, which, when the crystal is heated, causes it to split with a crackling noise, giving rise to what is called Decrepitation.

Some substances have so strong an affinity to the fluid in which they are dissolved, that they do not crystallize.

In some cases, their crystallization may be effected by adding to the solution a substance exerting an affinity to the fluid, and of course weakening its affinity to the solid it holds dissolved. The addition of alcohol promotes crystallization in this way.

As different bodies require different quantities of water for their solution, it is possible to obtain two such substances apart by crystallization, when they have been dissolved in one fluid; the one which is least soluble, or most disposed to crystallize, first passing to the solid form; and, by farther evaporation, the other being obtained. A fact rather singular is noticed by Kirwan, that if into a saturated solution of two salts in water, a crystal of either be put, that salt crystallizes in preference to the other.

Salts, the solubility of which in water is unequally promoted by heat, may also be obtained separately from the same solution by crystallization. Thus, if one salt be more soluble in hot than in cold water, and another be equally soluble or nearly so at any temperature, on evaporating the solution sufficiently, the latter salt will crystallize while the liquor is hot; the other will remain dissolved, but on cooling will shoot into crystals; and, by alternate evaporation and cooling, the two may be obtained, though generally with a little intermixture of each other. Sometimes, however, even when they have different tendencies to crystallization, their mutual affinity causes them to crystallize in one mass, and to assume a form different from that in which separately they would have crystallized. In other cases, this mutual affinity between substances in solution is able to resist their crystallization, or to render it more difficult, and sometimes the operation of crystallization seems to produce a change in the state of combination.

From these several causes the separation of salts by crystallization from a compound solution, even where it occurs to a considerable extent, is scarcely ever perfect. Each salt does not separate at a certain stage of concen-

tration, but the separation is considerably dependent on the proportions, and with the less soluble salt a portion of the more soluble generally separates. In evaporating, for example, a solution of Glaubers salt and of sea-salt, the former, which according to its solubility ought to remain in solution, separates even to a certain extent with the first crystals of the other. The higher the temperature, too, at which crystallization takes place, the more in general are the successive deposits mixed; hence by a slow evaporation salts are obtained more pure.

Crystallization sometimes takes place when bodies in the aërial form become subject to the attraction of aggregation, as is conspicuous in the crystalline arrangement of a flake of snow.

Solids separated from a liquid by chemical action, in some instances, in the moment of their separation, assume a crystallized form, usually, however, in minute grains.

The theory of crystallization is still obscure, so far as relates to the cause of the regular forms to which it gives rise. This has been accounted for, on the supposition that the particles of bodies have different figures, and that they have a polarity or a tendency to arrange themselves, in obeying the law of cohesion, by certain sides in preference to others; whence the uniformity of crystallization in each individual, and the difference in the figure of its crystals from that in others.

Every substance in crystallizing is disposed to assume a particular figure. Thus, sea-salt crystallizes in the form of a cube; nitre in that of a hexaedral prism. This, however, is not invariable, but may be altered by circumstances affecting the crystallization; and we find the same substance crystallized under a variety of forms. Sea-salt crystallizes not only in cubes, but also in octaedrons; and carbonate of lime is found in nature in the form of an hexaedral prism, an hexaedral, and a triedral pyramid, and in numerous other forms.

The numerous diversified figures of crystals may be reduced to others more simple, and the prosecution of this mechanical analysis has led to the development of the actual structure, and the theory of the production of a number of secondary from certain primary forms. Romé de Lisle had conceived this idea, and had shewn that the more complicated forms could be derived from those more simple, by the different truncations of which these are susceptible. To take the most simple example, a cube may be truncated in the direction of its sides, its angles, or edges. If the angles be cut off, we have no longer a figure of six sides, but of fourteen; if the edges be struck off, they will be replaced by twelve faces, and the figure will have eighteen sides; or, if the cube be truncated in the direction parallel to one of its faces, the equality of its sides will be destroyed, and a rectangled parallelopipedon be produced. In this manner De Lisle prosecuted the modifications of what he conceived to be the more simple forms. Those which he regarded as primitive are the tetraedron, the cube, the rectangular-octaedron, the rhomboidal parallelopipedon, the rhomboidal octaedron, and the dodecaedron with triangular faces*. These forms were, however, altogether arbitrary, and were selected merely from their supposed simplicity. Nor were the truncations less hypothetical, by which their transitions into secondary forms were explained. Haüy has developed more completely the structure of crystals, by detecting the primitive form by mechanical analysis, and has thus established a real instead of an arbitrary system of crystallography. Of this system it is necessary to give an outline, as important, not only in relation to the theory of crystallization, but from its application to mineralogy, and the discrimination of the mineral species.

Gahn observed, that in breaking a pyramidal crystal of

* Crystallographie, tom. 1. p. 74.

carbonate of lime, it afforded rhomboidal fragments, of which it appeared to be entirely formed. Bergman from this conceived the idea, that in every crystal there exists a primitive form, from which the actual forms may be generated, by the superposition of decreasing laminæ; and that, by the mechanical division of crystals, according to those joinings which yield most easily to a mechanical force, this form may be detected, and the laws by which it gives rise to the different crystals determined*. This is the basis of the system of Haüy, in which the particular laws of decrements are demonstrated, so as to shew how from these the secondary forms may be derived, and how the primitive form may be detected either by calculation or mechanical division.

The fact which led to these views is, that crystals can be mechanically divided only in certain divisions, so as to afford smooth surfaces. Thus, in a crystal of calcareous spar, a regular hexaedral prism, as represented in Plate I. fig. 1. and 2. †, if we endeavour to divide it parallel to the edges, which form the outlines of the basis of the prism, we shall find that three of these edges, taken alternately at the upper extremity, the edges *l f*, *d c*, *b m*, readily yield to a knife struck in the proper direction; but that the other three, those which are intermediate, *f d*, *c b*, and *m l*, cannot be divided in a similar manner; and if broken by a greater force, the fracture, instead of being polished, is rugged and uneven. If we repeat the experiment at the under extremity of the prism, we shall find here also, that segments of three only of the edges can be

* Physical and Chemical Essays, vol. ii, p. 1.

† In these and the other plates representing the crystalline forms, the entire lines represent the edges or outlines of that part of the solid immediately presented to view, and the dotted lines those situated in the opposite part, which of course are visible only in supposing the solid diaphanous.

detached; but these, instead of being the corresponding ones with those divisible at the upper extremity, that is, $l f$, $c d$, $b m$, are the intermediate ones, $f d$, $c b$, and $m l$.

The six divisions expose so many trapeziums. Three of these are represented in fig. 1., namely, the two which cut off the edges $l f$, $c d$, represented by the dotted lines $p p$, $o o$, and $a a$, $k k$, and that which cuts off the inferior edges, d, f , and marked by the dotted lines $n n$, $i i$. Each of them will have a smoothness, from which it can be perceived that it coincides with one of the natural joinings, the assemblage of which forms the prism; and the division cannot be effected in any other directions than these. But if the division be continued parallel to these segments, it necessarily happens, that, on the one hand, the surfaces of the basis of the prism become narrower, and, on the other, the heights of the sides diminish; and at the point at which, continuing the sections, the bases disappear, the prism will be changed into a dodecaedron with pentagonal faces (fig. 2.), six of which, $o o i O e$, $o I k i i$, &c. are the remains of the sides of the prism, and the other six, $E A I o o$, $O A$, $K i i$, &c. are the results of the mechanical division*.

Beyond this point, the planes at the extremities preserve their figure and dimensions, while the lateral planes continue to diminish in height, until the points o , k of the pentagon $o I k i i$ coinciding with the points i , i , and the other points similarly situated, having a like coincidence, each pentagon is reduced to a simple triangle, as is represented in fig. 3.

Lastly, by continuing the sections, the triangles are made to disappear, so that there remains no vestige of the surface of the original prism; but, in place of it, we have the

* In this and the two succeeding figures, the hexaedral prism which circumscribes the solid, extracted from it in the division, is still represented, to shew better the progress of the operation.

obtuse rhomboid E A I O, (fig. 4.), which is therefore the nucleus, or primitive form *.

This discovery of the method of dividing a crystal was made by Haiiy, in examining a crystal of calcareous spar, which had been detached from a group of which it formed a part. He observed, that the fracture had happened at one of the edges of the base of the prism, and that its surface was perfectly smooth and regular. Attempting to detach a segment in a similar direction from the contiguous edge, he could not succeed, but the one next to it was easily divided; and proceeding in this manner, he was able to effect the mechanical division of the crystal in the manner already explained. Struck with this important result of the experiment, he applied the same method to other crystalline forms of the same substance, and obtained from them the same result; the crystal, whatever was its figure, being by this mechanical division converted into a rhomb. Thus, in the dodecaedron of calcareous spar, composed of two six-sided pyramids, joined by the base, the primitive form may be obtained at once, by making a first section on the edges E O, O I, fig. 5.; a second on the edges I K, G K; a third on G H, E H; a fourth on O I, I K; a fifth on G K, G H; and a sixth on E H, E O; and the result is, that these edges become the same with the lateral edges of the primitive form, as may be perceived from mere inspection of fig. 6., which represents this primitive form inscribed in the dodecaedron. From other crystallized substances similar results are obtained; by discovering the joints by which the laminae composing the crystals are united, the primitive form may be extracted: from fluor spar, for example, an octaedron is obtained; from beryl, an hexaedral prism; and even from those that do not yield to this mechanical analysis, Haiiy has remarked, that their surface striated in a certain direction, or the relation subsisting among the secondary forms, af-

* *Traité de Mineralogie*, tom. i, p. 21.

ford indications which lead to the determination, with much probability, of the primitive form.

Such is the process by which Haüy establishes what he names the Primitive Form of Crystals. The forms hitherto observed are reducible to six :—the parallelopipedon, which includes the cube, the rhomb, and all the solids which are terminated by six faces, parallel two and two ; the tetraedron ; the octaedron ; the regular hexaedral prism ; the dodecaedron, with equal and similar rhomboidal planes, and the dodecaedron with triangular planes. The form is always the same in all the varieties of crystals of the same substance.

He carries the division of crystals farther, however, than the primitive form. The solid which constitutes it may be farther subdivided, parallel to its different faces, and sometimes in other directions. The enveloping matter is equally divisible, by sections parallel to the faces of the primitive form ; and the only limit to this possible division is that placed by the composition of the substance. Thus calcareous spar may be reduced to a particle, beyond which the division cannot be carried, without resolving it into its elements, lime and carbonic acid ; or, at least, it may be reduced to a particle, beyond which, if its minuteness allowed us to operate upon it, it is demonstrable its figure would not change. To these particles, the last result of the mechanical analysis, Haüy gives the name of *integrant particles*, and their union constitutes the crystal. Their forms, so far as experiment has been carried, are three : the tetraedron, the simplest of pyramids ; the triangular prism, the simplest of prisms ; and the parallelopipedon, the simplest of solids which have their faces parallel two and two.

The primitive forms and the figures of the integrant particles being determined, it remains to complete the theory of the structure of crystals, to shew by what arrangements the secondary forms, or actually existing crystals, are produced.

The nucleus of the crystal is the symmetrical solid which constitutes its primitive form, arising from the union of the integrant particles : the additional matter forming the crystal consists of layers of these particles, superadded to that nucleus, and arranged on its faces. To account for the formation of the crystal under a figure different from that of its primitive form, these layers, as they recede from it, are supposed to decrease in the space they occupy, from the regular abstraction of one or more ranges of the integrant particles ; and this taking place in various modes, different figures of crystals will be produced.

To take the simplest example, let it be supposed that the primitive form is a cube ; on each of its sides may be reared a series of decreasing layers, composed of cubical particles, each layer diminishing on each of its edges by one row of these minute cubes. The laminæ thus decreasing as they recede from the base on which they rest, until the apex consists of a single particle, a four-sided pyramid will be formed on each side of the cube. Two of these are represented, (fig. 7.), A B C D, E B C G.

We shall thus have six four-sided pyramids, and of course twenty-four triangles, such as A B C, B C E, C E G, &c. But since the decrease is uniform on all the sides, as from the line B C to A, and from the same line to E, it must also be uniform from A to E ; the side A B C of the one pyramid will therefore be found in the same plane as the side B C E of the adjacent pyramid ; so that the entire surface of these will be the rhomb A B E C. The case must be the same with all the others ; the twenty-four triangles will therefore be reduced to twelve rhombs, and the figure will be a dodecaedron, very remote from the primitive form. And although the representation in the figure be such as to shew the decrease of the laminæ, by rows of particles of such a size as to give a surface uneven, it is obvious, that if we substitute for this the delicate structure of nature, the number of laminæ may be so great,

and the minuteness of the particles such, that the channels at their edges will be imperceptible, and the surfaces will appear perfect planes:

Such is an example of the production of a secondary from a primitive form, by superposition of decreasing laminæ. The laws of decrement may be various. Häüy states four kinds: First, Decrements on the edges, or parallel to the sides of the primitive form, of which that described above is an example. 2d, Decrements on the angles, that is, decrements of which the lines are parallel to the diagonals of the faces of the primitive form. 3d, Intermediate decrements, or those which are parallel to lines situated between the diagonals and edges of that form. 4th, Mixed decrements, in which the number of ranges, abstracted in breadth or in height, give proportions, the two terms of which are beyond unity. These are farther liable to several modifications, according as the decrements take place on all the edges, or on all the angles, or on certain edges or certain angles only; or as they are uniform, by one, two, three ranges or more; or as the law varies from one edge to another, or from one angle to another. And sometimes even the same edge or the same angle undergoes successively several laws of decrement: Or the secondary crystal has faces parallel to those of the primitive form, which give rise to new modifications, from their combinations with the faces resulting from the decrements. With such diversity of laws, the number of forms that may exist is immense, and far exceeds what has been observed. Confining the calculation to two of the simplest laws, those which produce subtractions by one or two ranges, it is shewn, that carbonate of lime is susceptible of 2044 different forms,—a number fifty times greater than that of the forms already known; and if decrements by three and four ranges be admitted into the combination, the calculation will give 8,388,604 possible forms of the same substance. And even this number may be augment-

ed, in consequence either of intermediate or mixed decrements being taken into account.

To give a full view of the applications of these laws would require a statement inconsistent with the nature of this work. I refer therefore, for the details, to Haüy, *Traité de Mineralogie*, tom. i, ii. An ample abstract of the theory is given by the author in the *Annales de Chimie*, t. xvii., of which there is a translation in the first volume of the *Philosophical Magazine*; it is also explained in an excellent statement of it by Abbé Buée in *Nicholson's Journal*, vol. ix.

Mr Daniell has stated the important result, that the development of the mechanical structure of crystals may be sometimes effected by solution *. If a crystalline mass of a salt soluble in water be immersed in that fluid, or in a weak solution of the salt in water, its surface is soon acted on; but it is so unequally. "Striæ or ridges may be detected in various places, and indeed generally cover the whole of its superficies, which prove not only that the mechanical attraction of the solid has resisted chemical action, but that it has resisted it more in some directions than in others." And the rudiments of geometrical form may thus at length be observed. In a mass of alum, for example, subjected to this operation, the lower end of the mass presents the form of octohedrons, and sections of octohedrons stamped upon its surface. Borax produced crystalline forms not less distinct; sections of eight-sided prisms, with various terminations, being embossed on the mass, which in some directions were subdivided by lines parallel to the terminal faces into rhomboidal figures. Mr Daniell farther found, that substances not soluble in water might be made to afford similar results, from the action of other solvents, sufficiently moderated: calcareous spar, for example, from the action of vinegar, was, after a few days, marked with

* *Journal of the Royal Institution*, vol. i, p. 24.

lines on the surface, which by their mutual intersection presented the primitive rhomb of carbonate of lime: carbonate of barytes, and carbonate of strontites, by the action of the same solvent, were dissolved into hexaedral prisms: quartz was similarly affected by diluted fluoric acid: a mass of bismuth, subjected to the action of diluted nitric acid, exhibited on its surface, at the end of a few days, small cubic figures: antimony presented a series of rhomboidal plates; and nickel, at the end of a fortnight, was covered with perfectly defined regular tetrahedrons. Thus, by this method, if it is fully established, the arrangements constituting crystalline structure are evidently developed; it must be regarded as an important aid to mechanical analysis, and may be employed where the other is impracticable, or gives only imperfect results.

A more simple method of describing crystals than that of Haiüy has been given by Werner, and applied by him to mineralogical description. This, as being more conformable to common use, is adopted in the following work, and it remains to explain the terms and definitions connected with it.

The parts of which a crystal is conceived to be composed, are planes, edges, and angles. Planes, according to the usual geometrical definition, are surfaces lying evenly between their bounding lines; they are distinguished into *lateral*, which are those parts of the surface of the body which are of greatest extent, and which form its confines towards its smallest extent; and *extreme* or *terminal*, which are those of smallest extent, and form the bounds of the body towards its largest extent. Edges are formed by the junction of two planes under determinate angles; they also are *lateral*, or those formed by the junction of two lateral planes; and *terminal*, formed by the junction of two terminal planes, or of a terminal with a lateral plane. Lastly, angles are formed by the junction of three or more planes in one point.

Werner admits seven primary figures of crystals, with their modifications. These are, the icosaedron, the dodecaedron, the hexaedron which includes the cube and the rhomb, the prism, the pyramid, the table, and the lens.

1st, The icosaedron, Plate I. fig. 8., a solid, consisting of twenty equilateral triangular planes, united under equal angles: 2d, The dodecaedron, fig. 9., or solid, of twelve equal and regular pentagonal planes: 3d, The hexaedron or solid of six quadrilateral planes, including the cube, fig. 10., or solid, composed of such planes, united at right angles: and the rhomb, fig. 11., in which they are united at oblique angles: 4th, The prism, or solid of two terminal planes parallel, equal and similar, connected by quadrangular lateral planes, having one direction; the number of lateral planes may of course be various; the usual forms observed in crystals are the six-sided prism, fig. 12., the four-sided rectangular prism, fig. 13, Plate II., and the four-sided rhomboidal or oblique angular prism, fig. 14.: 5th, The pyramid, a solid, the base of which is a plane of an indeterminate number of sides, and the sides triangles, the vertices of which meet in a point; the more common varieties of this figure are the three-sided pyramid, or tetraedron, fig. 15., and the four-sided pyramid, fig. 16.: 6th, The table, which, strictly speaking, is a compressed prism; it is composed of two broad parallel lateral planes, and of an indeterminate number of terminal planes, connected with the lateral planes and with each other, and small compared with the lateral ones; the principal varieties are the rectangular four-sided table, fig. 17., the oblique-angular or rhomboidal four-sided table, fig. 18., and the six-sided table, fig. 19.: Lastly, The lens, fig. 20. a solid, consisting of two planes, which are curved; of which there are two varieties, one composed of two convex planes, another of a convex and a concave plane.

These primary forms are modified by combination, by truncation, by bevelment, and by acumination.

The modifications by combination are confined to the pyramid, two pyramids being joined by the base; the lateral planes of the one are either set *directly* on the lateral planes of the other, as in the double four-sided pyramid, or octaedron, fig. 21.; or *obliquely*, as in the double four-sided pyramid, fig. 22. Fig. 23. is the double six-sided pyramid.

A crystal is said to be truncated, when any or all of its solid angles or edges appear cut off, so that where there would have been an edge or angle, there is a plane. Fig. 24. shews the cube with the angles truncated: Fig. 25. the cube with the edges truncated: Fig. 26. the six-sided prism, with the terminal edges truncated.

A crystal is said to be bevelled, when its edges, angles, or terminal planes are so altered, that instead of an angle, edge, or terminal plane, there appear two smaller converging planes, which terminate in an edge. Fig. 27. shews the four-sided prism, bevelled on both extremities: Fig. 28. the cube with bevelled edges.

Lastly, The forms of crystals are altered by acumination. This is that kind of alteration, in which, in place of the angles, or terminal planes of a crystal, there are three or more planes converging, and forming a point or edge: Fig. 29. shews the cube, with the angles acuminated by three planes, set on the lateral planes: Fig. 30. the six-sided prism, acuminated by six planes, set on the lateral planes.

The forms of crystals from the preceding modifications are frequently altered, and rendered complicated, by being superadded or combined; and by the extent of the modifications, one form may pass into the other. They are likewise rendered complicated by aggregation, two or more crystals of the same substance being more or less closely united, from which aggregation arise various external forms.

CHAP. II.

OF CHEMICAL ATTRACTION OR AFFINITY.

WE are indebted to Newton for the first just views of the nature and extensive agency of this power. Besides those attractions which extend to sensible distances, "there may be others," he remarked, "which reach to so small distances, as hitherto escape observation." In conformity to this observation, he reviewed, in the 31st Query, at the end of his Treatise on Optics, and in some other dissertations *, a number of chemical phenomena, and considered them as arising from an attraction of this kind. When one body combines with another, he supposed this to arise from an attraction exerted from the particles of the one to those of the other; when they refuse to unite, it is because no such attraction exists; those which act with most energy are those, as he supposed, possessed of the strongest attraction; and when a compound is decomposed by the agency of another body, this he regarded as owing to an attraction exerted by that body to one of the principles of the compound, superior in force to the attraction which existed between them.

Geoffroy the elder conceived the idea of ascertaining the relative forces of affinity among different substances, by observing the order of the decompositions they produce, and gave the results of his observations in the form

* Letter to Mr Boyle on the Cause of Gravitation, and Observations on the Nature of Acids.

of tables. Pursuing the path which he had pointed out, succeeding chemists were occupied in observing these forces, as exerted by the principal chemical agents. The observations which had thus accumulated, were ably reviewed and corrected by Bergman. And Kirwan and Richter added some observations on the more obscure parts of the theory of chemical attraction. Bergman's views were received with little subsequent modification, and nearly the whole system of modern chemistry rested upon them. The researches of Berthollet, again, exhibited the subject under some new aspects. Other views equally novel and important have since been presented by Dalton, Wollaston, and Gay-Lussac, and form at present an interesting subject of discussion. The laws of chemical attraction cannot yet be considered as established with sufficient precision ; but I have endeavoured to place the whole subject under a few general divisions. In the first, I have premised some necessary definitions relative to attraction and its results. Under the second, I have taken a general view of the phenomena to which it gives rise. In the third is considered the operation of those circumstances by which its exertion is influenced, and its effects are modified. The fourth is devoted to the consideration of the limits which affinity observes. And under the fifth are placed the details which relate to the forces with which it is exerted. Under these divisions all the facts and doctrines relating to chemical affinity may be systematically arranged.

SECT. I.—*Definitions relative to Chemical Attraction, and its Results.*

CHEMICAL attraction may be defined, that force exerted between the particles of different bodies by which they are combined together. It is distinguished from Gravitation by not operating on masses of matter, nor at sensible distances, but being confined in its action to the minute particles of matter at distances altogether insensible. From cohesion it is distinguished by being exerted between particles not of the same nature, but of different kinds, and by forming therefore, from the union of these particles, not a mere aggregate, but a substance in which the properties of the bodies combined are more or less changed. The term Affinity has been introduced to denote this power, from an hypothesis once maintained, that some relation of resemblance exists between those bodies most disposed to unite. For this hypothesis there is no foundation, but the term is convenient, as opposed to that of Gravitation, and as synonymous with chemical attraction.

This force appears to be elective ; that is, it is not exerted indifferently by any body towards every other. Between many substances no mutual chemical attraction is apparent, or their particles cannot be brought into intimate union. It is uncertain, however, whether this is owing to their not having a mutual attraction, or whether it may not be ascribed to the predominance of circumstances by which attraction is counteracted. By each body, too, it is exerted towards a series of others, with different degrees of force ; and with regard to this also, there is reason to believe, that much of the difference is owing, not to real differences in the intensities of affinity, but to the operation of modifying circumstances.

The result of the exertion of chemical attraction be-

tween two or more bodies, is their intimate union, or assimilation into one substance, in which neither of them can be recognised, nor can they be separated from each other by any mechanical force. This operation is termed *Combination*. If we pour a quantity of water on common salt, the particles of the salt, though heavier than the water, will be attracted by it, and diffused through it, nor can they be again separated but by chemical agency. If we mix together a little lime and sulphur, and expose them to heat, a substance will be formed in which the two ingredients are intimately united, and the properties of which are totally dissimilar to those either of the sulphur or the lime. In both these examples, an affinity has been exerted between the substances concerned, and they have *combined* together. So intimately are the particles of the bodies which have been combined blended, that if the smallest portion of the substance they have formed be examined, it will be found to consist of the same principles united in the same proportions as the general mass; and by this union, the properties of both are altered, and new properties acquired.

Combination is to be distinguished from *Mixture*, in which dissimilar particles are intermingled, more or less intimately, but without being united by any attraction,—in which, therefore, no new qualities are acquired,—in which the difference of parts is easily discovered, and these parts are capable of being separated by mechanical means. It is also to be distinguished from *Aggregation*, which is the union of particles of the same kind of matter, forming an aggregate, uniform in composition, but possessing all the properties of the particles of which it is composed.

The substance resulting from chemical combination is denominated a Compound. It of course consists of two or more ingredients. These are named its Component or Constituent Parts. When these are separated from their union, the process is named, in chemical language,

Decomposition. Thus, chalk when exposed to heat is resolved into a peculiar elastic fluid, and into lime; and these are the ingredients of which it had been composed. When decomposition is effected with the view of discovering the constituent principles of a compound, it is named ANALYSIS. This may be of two kinds, either as effected by the application of heat, or by the intervention of a superior affinity. When exposed to a sufficient degree of heat, the attraction existing between the principles of a compound may be so far weakened that they separate; and one of them, being in general more volatile than the other, is expelled. Or, in other cases, a compound may not be decomposed by the most intense heat: but if it be mixed with some other chemical agent, and placed under circumstances favourable to the exertion of chemical attraction, the substance mixed with it may combine with one of its component parts, and the other may be obtained in an insulated form. These are examples of Simple or True Analysis. Complicated or False Analysis as it has been named, is that where the composition of the compound is subverted, and its individual existence destroyed, but where, from the combination of its principles in new modes and proportions, it is impossible to reproduce it by the union of the products of the analysis.

SYNTHESIS is the reverse of analysis. It is the reproduction of the substance, by the combination of the principles which the analysis discovers to be its constituent parts; and, when it can be effected, is regarded as the surest proof of the accuracy of the analysis. Thus, by combining lime and the peculiar elastic substance, noticed in the preceding illustration, a substance essentially the same as chalk is produced. When these operations of analysis and synthesis are combined in the investigation of the chemical constitution of any body, in other words, when we have resolved it into certain constituent prin-

ciples, and when, by combining these, we again form it, we obtain all the evidence which the science of chemistry can afford.

From the preceding definitions, it is obvious, that all the varieties of matter must, in a chemical point of view, fall to be considered as simple, or as compound. Either they must be resolvable into two or more different substances, from the union of which they have been formed, and in this case their composition is obvious, and they rank as compounds; or they must be incapable of such an analysis, and they are then regarded as simple or elementary. The great object of chemistry is to investigate the constitution of bodies—to determine what substances are simple, what compound; to trace the combinations into which the former are capable of entering; to decompose the latter, or discover of what constituent parts they are formed. And in chemical theory, Elements are not regarded as substances essentially simple, but merely as bodies which have not been decomposed.

Combination may take place between two or more simple bodies, but it may equally take place between compounds, the particles of the compounds as such exerting a mutual attraction. In such a case the compound formed may, under one point of view, be considered as composed immediately of the two compounds from the combination of which it has been formed, or it may be considered as composed ultimately of the simple substances or elements of which these consist. To facilitate the consideration of this, the distinction has been introduced of the *integrant* and *constituent* particles of bodies. The constituent or component parts or particles are substances differing in their nature from each other, and from the substance they form. The integrant parts are precisely similar to each other, and to the general mass which is composed by their union; or they are merely the smallest particles into which a substance can be resolved without decompo-

sition ; while decomposition is always implied in the division of a body into its constituent particles. The integrant parts are united by the force of aggregation, the constituent parts by chemical affinity. It is evident that simple bodies consist entirely of integrant parts, all their particles being alike. Compounds, again, may be considered as consisting both of integrant parts, and of component parts or dissimilar particles*. It has been supposed, that when an attraction is exerted between two compound substances, it is between their integrant parts, not their constituent principles, and that it is the combination of the former which constitutes the substance formed by their union. Berthollet has advanced the supposition, that an attraction exerted between two compounds is exerted from their constituent principles or elements, and is merely the sum of their attractions, modified by the state in which they exist in the combination ; an opinion, the probability of which we shall afterwards have to examine.

SECT. II.—*Of the General Phenomena which arise from the exertion of Chemical Attraction.*

THE exertion of an attraction between the particles of two bodies, is followed by their intimate union or combination ; and the most common and important result of such a combination is a change in the properties of the bodies combined.

* When the term particle is used alone in chemical language, it is generally in the sense of *integrant particle* ; and it ought perhaps to be restricted to this, to avoid the ambiguity arising from its use in any other sense.

This change is in many cases striking and complete, the properties of the substance formed by the combination being altogether different from those of the substances from which it has originated. The taste, smell, colour, form, density, and other physical qualities, and the chemical properties of fusibility, volatility, solubility, tendency to combination, and order of attraction in the compound, bear no resemblance to the same properties in its constituent parts. We cannot, therefore, from our knowledge of the properties of a body, infer with certainty what will be the properties of the compound formed by its union with another.

From this change being so general, it has been established as a law of chemical attraction, that *when chemical combination has taken place, the compound formed does not possess properties merely intermediate between those of its component parts, but has acquired others more or less new.*

This result of chemical attraction is of vast importance, since it is from it that the properties of the greater number of material bodies are derived. Almost all the productions of nature are compounds formed from the union of a few simple substances; and the numerous properties they possess, adapting them to so many purposes of utility, are derived from this source. They retain not the properties of their simple elements, for these must be comparatively few, but derive new properties from the arrangements into which their principles are brought when they are combined together.

The properties of bodies are not only changed by combination, but the kind and degree of change are influenced by circumstances connected with the combination, particularly by the relative quantities or proportions in which they are combined. Hence the same substances may, by combination in different proportions, form compounds, which are totally different from each other in qualities. The modes of combination, where three or more substan-

ces are combined, have a not less important influence. This it is difficult to illustrate with precision; but it is easy to conceive with regard to three substances, for example, that they may all exist in simultaneous combination, their affinities being mutually balanced; or two of them may be in immediate combination, and the compound they form may combine with the third. Or with regard to four substances, the modes of combination may be still more diversified, as either the whole may exist in mutual combination, or each of the elements may be combined with any of the others, and the compound thus formed may be farther combined with the compound formed by the union of the others. Hence, by merely changing the mode of combination, without any change either in the elements themselves, or in their proportions, products totally different may be formed.

Of the changes of properties from chemical combination, none is more common than change of form, or of the state in which bodies exist. If two airs are combined together, the result is often a substance in the fluid or solid state. Two fluids united may form a solid; and when a solid is combined with a fluid, the compound more frequently exists in the fluid than in the solid form.

This last case is so general, that a particular term has been applied to it in chemical language. Combination is the general term expressive of the union of substances from the exertion of mutual attraction; while the particular operation in which a solid is combined with a liquid, so that the liquid form is retained by the compound, is denominated Solution. It has been conceived, that in this case the liquid is the active principle; it is said to dissolve the solid; or the solid is spoken of as dissolved by it. The attraction, however, whence the combination proceeds, is reciprocal; and perhaps there is no propriety in the distinction of this from other cases of chemical union. It is generally applied to those combinations

where there are no important changes of properties ; and some have extended it so far as to apply it to all cases of chemical union, whether between solids, liquids, or airs, where the attraction has not been so energetic as to alter materially the properties of the substances united, but merely sufficient to overcome cohesion, elasticity, or any opposing force, and retain them united without any intimate approximation of their parts.

In solution, the affinity of the solvent is often so weak as not to give rise to any important alteration in the chemical relations of the body dissolved ; it is therefore neglected, and considered merely as communicating to it that fluidity which favours the exertion of its attractions to other bodies. It is frequently, however, sufficiently powerful to modify these attractions to a certain extent.

Though the change of properties from chemical action is often striking and important, it is not invariably so. In many cases the properties of one or both of the substances united can be recognised in the compound. In all the combinations, for example, of metals, with each other, the compound retains the general metallic properties. And in the solutions of salts, and of many vegetable and animal products, in water or in spirit, the properties of the substances dissolved, with the exception of the form, are scarcely altered. Yet these are real chemical combinations ; the substances are intimately blended, notwithstanding the difference of their specific gravities ; and their union is permanent, or they cannot be disunited but by the operation of heat, or the exertion of superior affinities.

From the consideration of this class of facts, the older chemists advanced the opinion, that the properties of compounds are intermediate between those of their constituent parts, or are at least derived from their elements. From this Newton deduced his singularly acute conjecture, that water contains an inflammable ingredient, founded

on its great refractive power. Stahl maintained the same opinion. As in the progress of chemical observation, however, many cases occurred in opposition to this principle, it was gradually relinquished; and the general fact merely stated, that in many cases of combination the properties of the bodies combining are not much changed, while in others the change is striking and complete, without this difference being referred to any principle. Berthollet has connected these facts, assigned causes for the peculiarities that are observed, and thus given a general theory of the change of properties from combination*.

The principle he assumes is, that the properties of compounds are derived from their elements, and would therefore be always apparent, but that they are often modified by circumstances attending the combination, so as to be materially changed.

One important modifying cause is the diminution which saturation produces in the strength of the affinities of bodies. One body combined with another counteracts, by the attraction it exerts to it, the attraction it might exert to a third. Hence the chemical action of a compound must be less energetic than that of its elements; and in the successive combination of compounds, the ultimate product is usually a substance which exerts very feeble affinities. On the same principle it may be inferred, that the elements of bodies must be substances which exert very powerful attractions. The general fact is well exemplified in the neutral salts, which have much less activity as chemical agents, and less tendency to combination, than either the acids or bases of which they consist.

Another circumstance, however, modifying this, is the condensation which attends combination, and which sometimes weakens the action of substances; in other cases adds to its force. The chemical action, for example, of

* Chemical Statics, Vol. i, p. 239.

substances existing in the aëriform state, is counteracted by their elasticity. Hence, if an elastic ingredient enter into a combination in which it exists in the liquid state, the action it exerts may be more increased by this condensation, than weakened by the affinity which is exerted to it by the substance with which it is combined in the compound. Of this we have an example in the acids; as in the nitric acid, where the chemical action, arising from the affinities exerted by the oxygen existing in it, is in many cases more energetic than that of oxygen in its aërial form. On the other hand, where condensation from chemical action is carried so far, that the elements in combining pass to a solid state, the cohesion acquired will concur with the diminution of their attractive forces from saturation, in limiting the affinities they exert, or in counteracting the affinities which may be exerted by others towards them; and such a compound will be less susceptible of chemical action than its constituent parts.

The same condensation may modify other chemical properties, as, for example, the relation of the body to heat: it may also change its mechanical constitution; and to the new arrangement of particles which an energetic combination occasions, may be ascribed the changes in colour, transparency, and other physical properties, which often attend chemical union.

Lastly, where opposing or incompatible properties exist in substances, these must be mutually weakened or destroyed, as in the example of the characteristic property of acids of reddening vegetable colours, and the equally characteristic one in alkalies of changing these colours to a green. One of these cannot be predominant in the compound, but from the other being impaired; and an equality of force will give rise to a state in which this as well as other similar characteristic properties of both substances must be lost. This is well illustrated in the combinations of acids with alkaline bases, and the formation either

of neutral compounds, or of compounds with acid or alkaline properties as either ingredient predominates.

The theory, therefore, may be maintained, that the properties of substances combining enter with them into the combination, and would always be discoverable in the compound, were it not for accompanying circumstances, by which they are modified or disguised, and from which apparently new properties are acquired.

Hence may be deduced the general rule, that where energetic affinities are exerted, or where substances having opposing properties are united, the properties will be much changed; but where the affinity exerted is less energetic, or where the substances combined are such as agree in the general assemblage of their qualities, the properties of the compound will not be far from those of its more active ingredient, or from the mean of those of its constituent parts. The first of these is well illustrated, in the solutions of salts in water. In this the affinity affecting the solution is not powerful, and is indeed little more than sufficient to counteract the cohesion of the solid; hence the only property that suffers alteration is the form. The combinations of the metals furnish an example which illustrates the second. They agree in the possession of a certain range of properties; and accordingly, when they are combined, the compounds have the general metallic qualities varied only, but in general not materially changed, so as to be far from the medium of those of the substances uniting; at least, not more than may be accounted for by the change in the force of affinity, and in the density which arise from the combination.

Even in those cases where more energetic affinities are exerted, and where substances with opposite characteristic properties are combined, we may often trace the properties of compounds, from those of their constituent parts, as in the examples of the ammoniacal salts, the volatility of which appears to be derived from their base; and in the

sparing solubility of salts, composed of ingredients which have a great tendency to solidity or fixity, compared with those which have tendencies of an opposite nature.

Yet, though these and similar facts accord with the theory, there are many for which, on the same principles, it would be difficult to account. To take an example which Berthollet himself has partly stated: Lime and magnesia with certain acids form salts which are deliquescent: potash and soda with the same acids form salts which have no such property; yet from the theory the reverse might be expected, as potash and soda are deliquescent substances, while lime and magnesia are not; so that if the property remain in the compound, it ought to be apparent in the salts having the two former for their base, not in those formed by the latter; nor is there any evident cause why in the salts of lime and magnesia such a property should exist*. Many other examples may be quoted. Thus the compound of lime with muriatic acid is deliques-

* Berthollet, in comparing these earths in this respect with barytes and strontites, which do not form deliquescent salts, ascribes the difference to "the influence of the capacity for saturation;" by which probably is to be understood, that as magnesia and lime saturate a larger quantity of acid than these bases do, the property of deliquescence may be derived from the acid, which, in the deliquescent salts that these earths form, has a strong attraction to water. But this larger quantity of acid which these bases condense, is supposed by Berthollet himself to denote a stronger attractive force which they exert; and, of course, this ought both to neutralize more completely any property of the acid, and produce a compound with more density or tendency to cohesion, and ought hence to prevent deliquescence, if this property were derived from the acid. And, ammonia, which has an attraction to water as great as soda or potash, is an example to which this solution does not apply; for it does not produce deliquescent salts, and yet, in capacity of saturation, it is even superior to lime.

cent; that with fluoric acid, so far from being so, is insoluble in water; yet as both acids have a strong affinity to water, and as they do not appear to differ much in the force of the affinity they exert to lime, there is no apparent cause for this difference. The whole class of salts, indeed, might be passed under review, and as many would be found unfavourable, as favourable to the theory.

There are also properties observed to be acquired by compounds, for the production of which it would be difficult to give any explanation. Suppose, that the characteristic properties of acids depend, as has been supposed, on their oxygen, from what modification can arise the most characteristic quality possessed by all of them, that of changing the vegetable colours to a red, a property not observed in oxygen? Or whence can the opposite property of the alkalies, that of changing the vegetable colours to a green, derive its origin? At the same time it must be admitted, that a slight circumstance may give rise to apparent difficulties, and that in such cases we cannot be assured that all the modifying circumstances are precisely known. We can scarcely expect more in the theory, than that it shall accord with the greater number of facts; and if there are some which appear to be not comprehended under it, or even to be in opposition to it, this may arise rather from the difficulty of the investigation, than from the principle itself being false.

In chemical combinations, there is in general one change which, being apparent, even in those cases where the changes of properties are least considerable, has been regarded as a test of chemical union,—an alteration of density; the density of the compound not being the mean of the densities of the component parts, and the deviation from this mean being often considerable. In the greater number of cases, it is increased, or a mutual penetration attends the combination. Where two airs, by combining, pass into the fluid state, or when two fluids, or a fluid and

solid, form a solid compound, this is necessarily the case to a great extent, and often the density not only exceeds the mean, but exceeds much that of the more dense of the combining substances : in this case the great condensation is, properly speaking, the consequence of the change of form. But even where this does not take place, the density is increased, though not to the same extent. Thus, if ardent spirit, of the specific gravity of 825, be mixed with an equal weight of distilled water, the specific gravity of which is 1000, the density of the fluid resulting from the combination is not the mean density 912.5, but is 930. There are many similar examples in the combination of saline substances with water.

A fact on this subject, somewhat singular, was observed by Kirwan, that in combinations the increase of density does not immediately acquire its *maximum*, but continues to increase. Thus, in combinations of sulphuric acid, or of nitric acid with water, the full density is not attained after the heat arising from the mutual action has been reduced, and the fluid has attained the temperature of the surrounding medium ; but after the mixture had remained six hours, a time more than sufficient to cool it, it still continued to increase ; and in combining one part of sulphuric acid with two of water, twelve hours at least were requisite to the combination attaining its full density *. It can scarcely be doubted, however, but that in this case the combination becomes gradually more intimate.

Another anomalous fact with regard to these combinations is, that the increase is greater when the bodies are combined at a low than when combined at a high temperature. This was ascertained by De Luc to be the case with alcohol and water, and by Dr Crawford to hold true with sulphuric acid and water †.

* Philosophical Transactions, vol. lxxii, p. 180.

† Treatise on Heat, p. 480.

Though there is a tendency to increased density from combination, this is not always apparent; it is sometimes even diminished. In every instance, perhaps, in which two liquids combine, the density is increased; but when a solid is dissolved by a liquid, an enlargement of volume is sometimes observed. Now, as in chemical combination, the particles of two bodies are made to approximate, it is not very obvious how enlargement of volume should be produced. This has been very well explained by Berthollet: A body in passing from the solid to the liquid form generally has its volume enlarged: in solution, therefore, the augmentation of volume which the solid acquires, by passing into the liquid state, may be greater than the condensation resulting from its combination, and, on the whole, diminution of density be the result. It is not confined, however, as Berthollet has represented, to those cases in which there is a change of form. In many of the combinations of the metals, the compound has a specific gravity inferior to the mean specific gravity of the metals combined, though it exists in a solid state. In these cases, it is probable, that the enlargement of volume which happens, arises from a crystalline arrangement, and is similar to the increase of volume which attends the congelation of a number of substances.

In the combination of ærial fluids, some important general laws exist with regard to condensation, which were first pointed out by Gay-Lussac. In general, when two airs combine together, and the product remains in the ærial form, the condensation bears a certain simple proportion to the volume of airs, or rather to that of one of them. Thus, it is sometimes exactly equal to the volume of one. An example of this is to be found in the combination of carbonic oxide gas and oxygen gas; they combine in the proportion of 100 parts by volume of the former with 50 of the latter; the product, carbonic acid gas, occupies a volume exactly equal to 100: here, therefore, the conden-

sation is equal to that of the volume of oxygen gas. Nitrogen gas combines with oxygen gas in the proportion of 100 volumes with 50, to form nitrous oxide; and the volume of the nitrous oxide, there is reason to believe, is 100: the condensation in this case also, therefore, is exactly equal to the volume of the oxygen gas. The same proportion appears to exist in the combination of oxygen and hydrogen gases, forming watery vapour, though from the difficulty of ascertaining exactly the specific gravity of steam, it cannot be affirmed with perfect certainty. In other cases the ratio of condensation is different. Thus, three volumes of hydrogen gas combine with one volume of nitrogen gas, forming ammoniacal gas; and from the specific gravity of this gas, it follows, that the condensation is exactly half of the whole volume, or twice the volume of the nitrogen. The same proportion is found in the combination of muriatic acid gas and oxygen gas. Lastly, there is reason to believe, that in some cases no condensation occurs. The density of nitric oxide gas is very nearly conformable to this, supposing it to be composed of equal volumes of oxygen and nitrogen gases*.

Another law is observed with regard to condensation in the compound of an aëriform substance with a body in the solid form, the product of their combination remaining aërial. In this case it frequently happens that there is no sensible condensation; the new elastic fluid continues to occupy exactly the volume of the other, and its increased density, therefore, is just that which it gains from the solid combined with it. Thus, when oxygen gas combines with charcoal, its volume remains unchanged; the new elastic fluid, therefore, which is produced by this combination, carbonic acid gas as it is called, is just so much heavier than the oxygen gas, as the weight of the

* Mémoires d'Arcueil, tom. 2, p. 218.

charcoal combined in it amounts to. In the same manner, when the aëriform fluid named hydrogen combines with sulphur, there is no change of volume ; and the same law is probably observed in the combination of sulphur with oxygen, forming sulphurous acid. It may be supposed, in these cases, as Gay-Lussac suggests, that the law comes under that case of the combination of two airs in which the condensation is that of the volume of one of them ; the solid in passing into combination with the air may be supposed to pass into the aërial form, and the condensation attending the combination may be exactly that of its own volume.

Next to the change of properties, the most important phenomenon attending chemical action is change of temperature, in other words, the production either of heat or of cold. And so general is this effect, that it has been stated even as a law of chemical attraction, that *its exertion is accompanied by a change of temperature.*

The production of heat is the more frequent change ; and the great source of heat in the operations of art is chemical combination. The heat evolved in combustion, in fermentation, and from the mixture of different chemical agents, has this origin. The production of cold takes place in the solutions of salts in water, or in other fluids which act upon them with more energy than water does. It also occurs to a still greater extent, when salts act on ice or snow ; and the greatest colds we can produce arise from these combinations.

This production of heat and cold is owing to a change in the relation of the substances combined to the principle on which temperature depends, expressed by saying, that by chemical combination the capacities of bodies for heat are altered, a subject to be afterwards considered. But there is a less abstract view, referring to the immediate causes given by Berthollet, of which the following is a sketch.

The effect of chemical combination is condensation, or there is an approximation of particles, whence the compound occupies less volume than its constituent parts. Now condensation is always accompanied with an evolution of heat, as is perceived distinctly in the rise of temperature produced by reducing the volume of an elastic fluid by mechanical pressure. And the effect must be the same, when the condensation is the effect of chemical action. The connection between these was accordingly so obvious, that it could not escape observation. It could not fail, however, to be also remarked, that the degree of heat produced is not proportional to the degree of condensation, but in some cases is greater, as measured by that condensation, than in others; and the opposite change, or the production of cold, although it is connected with enlargement of volume, is likewise not found to be proportional to that enlargement. There must therefore be some circumstance by which this is modified. This is the transition of form which so frequently accompanies combination; a liquid becoming solid, or an air becoming liquid, or the reverse of these changes taking place. A change of form is of itself, and independent of any alteration of density, accompanied with an evolution or absorption of heat; the absorption taking place when a solid becomes liquid or æriform, and the evolution when an æriform substance passes to the liquid, or a liquid to the solid state. In chemical action, therefore, we have two causes producing change of temperature, and modifying each other,—condensation, and change of form; the effect of the former being to produce heat, and that of the latter, according to the kind of change, to produce either heat or cold: the one therefore will sometimes counteract, sometimes concur with the other.

Thus, in the case of a liquid acting on, and dissolving a solid, condensation is the immediate effect of the combination, and so far is productive of heat. But the transition

of the solid into the liquid state is a source of cold ; this generally exceeds the other effect, and hence, in solutions, actual cold is the usual though not invariable result. In some energetic combinations causing solution, considerable heat even is produced, the condensation from the combination being more than sufficient to counterbalance the effect from the change of form. In like manner, the evolution of a substance in the aërial state produced by chemical action, will, as a source of cold, counteract the effect from the condensation resulting from the combination, and lessen the degree of heat that would have been excited ; yet still the latter circumstance may be sufficient to furnish, not only the heat required for the constitution of the aërial fluid, but to render a portion sensible, and raise the temperature. In the reverse cases, the results are similar. If the effect of chemical action is the transition of a substance from the aërial to the liquid, or from the liquid to the solid state, this will co-operate with the increase of density which attends the combination, and will cause more heat to be evolved than that increased density by itself could have produced. We find too, that heat, more or less considerable, arises from the combination of two liquids ; because even although the combination be feeble, there is always some degree of condensation, and there is no change of form to produce an opposite effect ; and where the condensation is considerable, as in the combination of sulphuric acid or of alkohol with water, the rise of temperature is very observable.

These two causes, change of density and change of form, thus modify each other in the production of change of temperature from chemical combination ; and it is requisite not merely to consider the total variation of density, from whatever cause it may arise, but the effects of each. For by change of form new relations to the principle or cause of heat are acquired, in consequence of the new arrangements of the particles which are produced ; and

these are independent of the alterations in density which may happen at the same time. Hence, in giving the theory of change of temperature from chemical action, the circumstances of change of density from the combination and change of form from it must both be taken into view, and it is by doing so that we are enabled to explain the fact not otherwise accounted for,—the connection of the production of heat in chemical combination with increase of density, and of the production of cold with diminution of density, while at the same time they are not proportional to each other. It must also perhaps be admitted, that in different bodies a change of density, to an equal extent, will be productive of different degrees of heat or cold, from the different relations they have to the principle on which temperature depends; and although it is so far satisfactory to trace the immediate causes, the phenomena must, as has already been remarked, be ultimately referred to the changes of capacity for heat, as ascertained by experiment.

SECT. III.—*Of the Circumstances by which Chemical Attraction is influenced.*

CHEMICAL Attraction is not an invariable force, which, as it is exerted by any body, operates in all cases with the same strength. Its operation is considerably dependent on certain qualities of bodies, or on certain circumstances under which they may be placed. These are, the relative quantity in which one body acts on another; the cohesion of bodies; their insolubility in any fluid which is the medium of action; their specific gravity; efflorescence; elasticity; and the state of temperature. The influence of some of these circumstances had been long known; that of others has been more clearly illustrated, and in some respects placed under a different point of view, by the re-

searches of Berthollet. Yet there still remains considerable uncertainty with regard to some parts of the subject. The influence of the relative quantity in which one body acts on another may first be considered, as it modifies, to a certain extent, the operation of the others.

I. QUANTITY OF MATTER.—The influence of this circumstance on the exertion of chemical attraction has been presented under different points of view, leading to conclusions which are in some measure opposed to each other. It will be proper, therefore, first to consider the subject as strictly as possible according to the actual facts, and then to state the principle according to which these may be illustrated.

It has been long known, that when two bodies combine together in different proportions with regard to each other, the attraction is stronger, in some of these proportions, than in others. Considering one of the substances as the base of the combination, and taking it in a fixed quantity, and considering the other as combined with it in different proportions, and as the substance which is to be more peculiarly acted on by a decomposing force, whether that of heat, or of another affinity causing its abstraction, it is found to be abstracted with different degrees of facility, in these different proportions. In that proportion in which the largest quantity of the base is present, that is, in the first proportion of the other ingredient, the decomposition is effected with greatest difficulty, while the abstraction of the additional proportions of the latter is effected with comparative facility. The large relative quantity of the base, therefore, seems to add to the force of attraction, which it exerts in opposition to any power expelling or abstracting the other. The observation of this led to the expression of the partial law, that attraction is in the inverse ratio of saturation, or that the first portions of a

body combined with another are retained by it, by a more powerful attraction than any additional portions.

Numerous illustrations of this general fact might be given. Metals, for example, combine with oxygen generally in two, sometimes in three or in four proportions. Now the abstraction of the oxygen from these compounds, either by the action of heat, or the attraction exerted to it by another body, is easily effected to that extent in which the larger proportions of it are present, while the entire abstraction, or, in other words, the abstraction of the first proportion, is often extremely difficult; that is, if 100 parts of a metal combine in one combination with 10 of oxygen, and in another combination with 20 of oxygen, 10 parts of oxygen in the latter compound will be easily abstracted, while the other 10 parts, or that proportion which constitutes the first compound, will be retained by a much more powerful force. Sulphur combines with two proportions of oxygen; the larger proportion which exists in one of these is easily abstracted, while the entire quantity is abstracted with more difficulty. Charcoal and oxygen afford a similar example. In like manner, in saline compounds, the base of the combination, an alkali or earth, is often combined with different proportions of an acid, and in all such cases the first proportion, that is, the smaller quantity of the acid which is combined with the base, is held in union with a stronger attraction than any of the additional proportions. So far, therefore, the effect of quantity is evident.

Another general fact, proving the influence of relative quantity of matter on the force of attraction, in some measure belonging to the former, though not altogether limited to cases where definite proportions are established, is the difficulty of entire decomposition either by the operation of heat or of a superior attraction. Thus, in the case of the compounds of aëriform bodies with bodies which are fixed, the aërial ingredient can often be partially expelled by

heat, while its entire expulsion cannot be effected. The same fact is exemplified in decomposition effected by divellent affinities. When a base of sparing solubility is precipitated from a combination, by the attraction exerted by another body to its solvent, it often retains a portion of the ingredient with which it was combined, as in the decomposition of metallic salts by an alkali; the metallic oxide, the base of the salt, often retaining a portion of the acid with which it had been united. In all these cases it appears, that as the decomposition proceeds by the expulsion or abstraction of one of the ingredients, the relative quantity of the other ingredient being increased, adds so much to the force of attraction which it exerts, that the progress of the decomposition is arrested. Nor is this limited to cases where definite proportions are established; it occurs in those in which the combination is indefinite, or in which at least attraction is less strictly limited; and even in those where definite proportions do exist, minute quantities of an ingredient (inferior to the quantity which constitutes the first determinate proportion) appear to be often retained with great force.

The influence of the relative quantity in which one body acts on another, in the force of attraction which it exerts, is farther demonstrated by the general fact, that in decomposing a compound by the action of a substance exerting an attraction to one of its ingredients, an increase in the quantity of that substance beyond that which forms the most powerful combination of it with the other, often renders the decomposition more perfect. In the case of a salt, for example, composed of an acid and a base, combined in the proportion which constitutes neutralization, if it is to be decomposed by the action of another acid, it is often necessary or advantageous to add a larger quantity of this acid than is sufficient to produce neutralization in the new compound, and this larger quantity evidently adds to the force which it exerts, so as to render the de-

composition more perfect*. Nay, in many cases the mere addition of a larger quantity of a body will enable it to decompose a compound by the attraction it exerts to one of its ingredients, while in a small quantity it will have no decomposing effect whatever. Thus, in metallic solutions, there are many of them to which a certain quantity of water may be added, without any decomposition being produced; while, if the quantity of water be increased, it abstracts from the metallic base a portion of the acid, and precipitation from this decomposition is produced. And it is of importance to remark, that in these cases there is no limitation in the progress of the decomposition, no successive formation of two or more definite compounds. The addition of a small portion of water has no decomposing effect: if a little more be added, the transparency still remains: with a farther addition, it begins to be impaired: by continuing the addition, the metallic oxide is deprived of more and more of its acid, becomes more insoluble, and renders therefore the liquor more turbid; and by the affusion of a sufficient quantity of water, nearly the whole of the acid may be abstracted.

Another important fact, establishing the same general conclusion, is one which has been noticed by chemists under the name of Reciprocal Attraction. A compound of two bodies, A and B, may be decomposed by the attraction exerted by a third body, C, to one of its ingredients, suppose to A; the other ingredient B is disengaged, and a new compound AC is formed. In this case it could not be supposed that the compound AC would be again decomposed by B; but such is the fact: by peculiar arrange-

* A practical exemplification of this is in the decomposition of nitre by sulphuric acid, to afford nitrous acid; a larger quantity of sulphuric acid being employed with advantage than is necessary merely for the saturation of the potash of the nitre.

ments it may be decomposed to a certain extent by the action of B, and a portion of the compound AB reproduced. And the arrangement for this purpose consists merely in bringing a large quantity of B into action. The example in which this was particularly observed was that of the decomposition of the compound of sulphuric acid and potash by nitric acid. Common nitre, the compound of potash and nitric acid, is easily decomposed by sulphuric acid, the sulphuric acid combining with the potash, and disengaging the nitric acid. Yet, on submitting the compound of sulphuric acid and potash to the action of a *large quantity* of nitric acid, it was found that the latter attracted a portion of the potash, and a quantity of nitre was reproduced. There are similar results in the mutual action of sulphuric and muriatic acids in soda; and indeed in a number of examples in the mutual action of acids and bases, and they all afford what is apparently a very direct proof of the effect of the quantity in which a body acts on the force of affinity it exerts. Bergman gave a very ingenious explanation of it somewhat different, but which leads to the admission of the same principle to a certain extent—an explanation which I shall have immediately to consider.

Lastly, in consequence of the attraction exerted being modified by the relative quantity within the sphere of action, there are many cases in which, when a body is brought to act in opposition to another on a third substance to which both exert attractions, the latter is not exclusively combined with either, but unites in different proportions with each, and thus two compounds are formed. Now it is obvious, that if attraction were an uniform force acting simply according to its intensity, this should not happen. The body exerting the most powerful attraction to the third substance ought, if a sufficient quantity of it to form the proportion in which they unite be present, to combine with it exclusively, and the other exerting the weaker af-

finiteness ought to remain uncombined; while, if affinity is modified by the quantity present, then a certain portion of the third substance must enter into combination with the latter, and the proportion in which the participation is established will be in some ratio of the affinity and quantity of each. There are accordingly many cases in which this happens;—in saline compounds, in particular, when two acids are brought to act on a base, each of them combines with a certain portion of it; or when two bases act on one acid, a similar participation of it takes place. These cases were amply illustrated by Berthollet, and confirmed by experiment. A few of the more striking will be found in a note *.

“I have kept,” says Berthollet, “an equal quantity of potash, and of sulphate of barytes, in a small quantity of boiling water. The potash had been prepared by alcohol, and contained no carbonic acid. The operation was performed in a retort, and consequently in communication with the air; and it was continued until the mixture was desiccated: the residue was washed with alcohol, which dissolved the potash, and after that with water, which also produced an alkaline solution, the alkali of which saturated with acetic acid; after which, by evaporation, the solution yielded crystals, possessing all the characters and qualities of the sulphate of potash. Whence it appears, that the sulphate of barytes was partially decomposed by the potash, and that the sulphuric acid was divided between the two bases.” Now barytes decomposes with facility the compound of sulphuric acid and potash, by attracting the acid; yet here again potash, when employed in large quantity, takes a portion of the acid from barytes. “Sulphate of potash,” says Berthollet, “having been submitted to a similar experiment with an equal weight of lime, and the dried residue having been treated with alcohol, an alkaline solution was produced: and a part of the residue dissolved in water, and yielded a small quantity of sulphate of lime along with the sulphate of potash.” Here the conclusion is similar, for sulphate of lime is decomposed by potash, yet we find that

Such are the various facts having a relation to the influence of the relative quantity of a body on the chemical action which it exerts. It remains to consider the expression of the law under which they are to be explained.

Berthollet, by whom they were first clearly illustrated in all their extent, supposed the attractions exerted by bodies to be in all cases modified by the relative quantities of them, within the sphere of action. He considered chemical attraction as a force, which is capable of being exerted between bodies in all proportions; limits to particular proportions in their combinations, when they do occur, being established only from the influence of the external forces of cohesion, elasticity and others. Where such cir-

sulphate of potash can also be decomposed by lime. In the same manner, oxalate of lime was decomposed by potash, phosphate of lime by potash, carbonate of lime by potash, and sulphate of potash by soda. In all, it is evident, "that the bases which are supposed to form the strongest combinations with the acids, may be separated from them by others, whose affinities are supposed to be weaker, and that the acid divides itself between the two bases. It also appears, that acids may be partially separated from their bases by other acids, whose affinities were supposed to be weaker; in which case, the base is divided between the two acids." (*Researches into the Laws of Chemical Affinity*, page 8, 9, &c.)

Some facts have been stated in opposition to these, principally by Pfaff, (*Annales de Chimie*, tome 77.) He found, that decompositions, in various cases of saline substances, were complete without any participation whatever, though the effect could not be ascribed to the operation of any external force; and in other cases decompositions were not obtained even when a large quantity of a decomposing substance was employed. Berthollet has shewn, however, that in these cases circumstances operate, the influence of which was not perceived. This is to be stated more fully in considering the relation of these facts to the doctrine of elective attractions.

cumstances, therefore, do not operate, the tendency of attraction is to cause combination in every proportion: it is exerted between different bodies in different degrees of strength: it is also influenced by quantity, so far, that an increase of quantity may always be made to compensate for a weakness of affinity; and the law which regulates chemical action in conformity to these views is, that "every substance having a tendency to enter into combination acts in the ratio of its affinity and quantity."

The general proposition on which this conclusion rests, that of unlimited attraction, cannot however be maintained. There evidently appear, in many cases, to be limits to combination, independent of the operation of external forces, and as the immediate result of the operation of attraction itself; bodies combining more powerfully in certain relative quantities than in others, and their combinations being hence established not only in these proportions but in no others. Of course, therefore, the influence of quantity on the force of attraction cannot be admitted to an indefinite extent; for if the quantity of any body exceed that proportion in which it is disposed to combine with another, it can evidently have no effect, nor can any effect arise from quantity in any proportions intermediate between those to which the combination is limited. There are accordingly many cases, in which increasing the quantity of a body seems to add nothing to the energy of its chemical action.

In these combinations, therefore, the expression of the law must be restricted to the general proposition before enumerated, that the strength of combination is different in different proportions, and that considering one of the bodies as the base of the combination, from which the other is to be abstracted by some divellent force, the resistance which the base opposes to that force is greatest in that combination, in which it is in the largest relative quantity to the other.

It has been supposed that the influence of quantity operates no farther than this; and the other facts apparently establishing it to a greater extent, so far as they are admitted, have been attempted to be brought under this expression of the law. With regard to some of them the explanations thus given are not improbable. Thus, the general case of reciprocal affinity was originally explained by Bergman, with much ingenuity, on a principle which may be rendered conformable to it. He supposed that a compound might have an attraction to an additional portion of one of its ingredients, and that this might aid its decomposition to a certain extent when it is acted on by a substance exerting an attraction to its other ingredient. In the example already referred to, (page 80.) of sulphate of potash decomposed by nitric acid, Bergman conceived that this compound exerts an attraction to an excess of one of its ingredients, sulphuric acid; when acted on therefore, by nitric acid, two forces operate to produce its decomposition,—the attraction of the nitric acid to the potash of the sulphate of potash, and the attraction of the sulphate of potash to an excess of sulphuric acid. At the same time that decomposition must be partial; for when the sulphate receives, in the progress of the operation, the quantity of sulphuric acid to which it has an affinity, there remains only the attraction of the nitric acid to the potash, which of itself is unable to prevail. The results, therefore, are the combination of the potash of a certain portion of the sulphate of potash with the nitric acid, while the sulphuric acid of this portion combines with the remaining quantity, and forms what is called super-sulphate of potash. Now, it may be supposed, that this proportion of sulphuric acid is a determinate one, and also that it is directly combined with the potash; in other words, that potash combines with sulphuric acid in two definite proportions; and then the case may evidently be

expressed in conformity to the preceding general law. Other cases of reciprocal affinity, such as that of the compound of sulphuric acid and soda, decomposed by muriatic acid, may be explained in the same manner: and Bergman remarked, that with regard to many saline substances, there are thus exerted attractions sometimes to an excess of acid, and sometimes to an excess of base.

In cases too, in which decomposition is promoted or rendered more perfect by an increase in the quantity of the decomposing substance, the same principle may be applied. In that, for example, already referred to, of the decomposition of the compound of nitric acid and potash by sulphuric acid, in which it is found, that to produce the entire decomposition, a larger quantity of sulphuric acid must be added than is necessary to saturate the potash; this larger quantity may be conceived to operate by forming the definite compound of potash with an excess of sulphuric acid, and thus preventing the concurrent affinity explained in the preceding paragraph, by which otherwise a portion of nitric acid would be retained in combination with a corresponding portion of potash.

The cases of partial decomposition, from the agency of a decomposing force, have in like manner been referred to the principle, that successive definite compounds are formed, in which the force of attraction is different in different proportions. Thus, when the compound of potash, with the largest proportion of carbonic acid with which it unites, is exposed to heat, a considerable portion of carbonic acid is expelled by a heat comparatively moderate, while the expulsion of the entire quantity requires a heat much more intense. In this case the potash is considered as combined with carbonic acid in two definite proportions; in one of which, that containing the smaller proportion, the force of attraction, conformable to the general law, is much stronger than in the other; and hence it re-

sists the decomposing force by which the compound in the other proportion is decomposed.

Some of these explanations are probably just, and wherever combinations in definite proportions truly exist, this expression of the law ought to be applied. But there is some reason to believe, that the assumption of definite combinations, to the exclusion of the influence of quantity, has been too far extended, that there are cases in which they do not exist, and in which that influence must be admitted with less limitation.

In the decomposition, for example, by heat, of compounds, composed of a fixed and volatile ingredient, in which the volatile ingredient is expelled, there appears, in many cases, to be nearly an insensible gradation in the decomposition, according to the degree of heat applied, and this even in compounds in which, under other circumstances, the elements combine in definite proportions. Carbonate of lime, the compound of lime and carbonic acid, affords an example. It yields different portions of carbonic acid according to the degree of heat to which it is exposed; and the last portions are retained with such force, that a very powerful heat is required to expel the whole. Now, on the doctrine of definite proportions, the decomposition should either not take place, or when it occurs it should be complete; or at least, if there is any intermediate state, this should be limited to one or two specific proportions. But the fact is otherwise: variable quantities of carbonic acid may be expelled, variable quantities of course remaining; and the influence of quantity through the whole operation is evident from the fact, that a higher heat is necessary to cause the expulsion as the decomposition proceeds. The only mode of accounting for this on the other assumption is, that a portion only of the carbonate is decomposed, another part of it remaining undecomposed. But how is this possible, since the whole mass is equally exposed to the same tempera-

ture, and must undergo therefore the same change. And the fact is a proof, that even with regard to substances, which usually combine in uniform proportions, others may be established, and this from the influence of quantity alone. There are many similar facts ; in almost all cases, indeed, of decomposition by heat, the expulsion of different portions of the volatile ingredient takes place at successive stages of temperature, and nothing frequently is more difficult than to produce its perfect expulsion. In decompositions produced by the operation of divellent affinities, there appear to be also, in many cases, a series of indefinite combinations established. In decomposing, for example, a metallic salt by the action of an alkali attracting its acid, the decomposition is often only partial ; that is, the metallic oxide which is precipitated retains a portion of the acid combined with it, more of the acid being abstracted as a larger quantity of alkali is brought to act on the precipitate. Nor is there any thing but assumption in the supposition which has been advanced to account for this, that these precipitates are *mixtures* of two or more definite compounds. In like manner, in abstracting carbonic acid from potash by a divellent affinity, such as that by lime, it is scarcely possible to abstract it entirely. If therefore definite combinations are supposed to exist in these cases, they must be held to be much more numerous than has usually been maintained.

Lastly, in combinations which are admitted to be altogether indefinite, the influence of quantity on chemical attraction is equally to be traced. Sulphuric acid and water combine in all relative proportions to each other. But the energy of action is much greater when a given quantity of the acid is combined with a small portion of water, than when it is combined with a larger quantity. And in again expelling the water by heat, a higher temperature is required as the quantity of water is reduced ; in other words, as the acid is relatively increased. When

water is brought to act on a solid salt, a large quantity overcomes the cohesion of the solid with facility and dissolves it; but as this proceeds, the quantity of solid matter dissolved becoming larger, the affinity becomes weaker; the solution takes place more slowly, and at length ceases. In all these cases then, the energy of chemical action is increased, simply by the increase of quantity in the body exerting it, independent of any law with regard to specific proportions.

The general summary then, which may be given with regard to the influence of the relative quantity of matter on the attraction which bodies exert, is, that in those combinations in which proportions perfectly definite are established, its operation is limited to these proportions. This necessarily must be the case; but still its influence is conspicuous in the general fact, that the resistance opposed to decomposition is different in the different proportions, and is greatest in that proportion in which the smallest quantity of the ingredient acted on by the decomposing force is present, the larger relative quantity of the other adding to the attraction it exerts. In combinations which are less strictly definite, its effect is more general, and is often evident in partial decompositions, and in the participation of a body acted on by others exerting an attraction to it under the same sphere of action. Lastly, in combinations which are unlimited, its operation is still more simple, and may perhaps be expressed, according to the annunciation by Berthollet, that the energy of action is in the ratio of the affinity and quantity of the body exerting it. And in all these cases, the influence of this circumstance can often be happily applied to the explanation of chemical phenomena.

As all attraction is mutual, it is necessary, in expressing the effect of quantity in the combination of two bodies, to consider it in relation to the force which is exerted to subvert the combination. If in a compound of *a* and *b*, the

force exerted is one acting more peculiarly on a , and tending to abstract it, as, for example, the attraction of another body towards it, or the effect of heat upon it, as a volatile substance, compared with the other as fixed, then the influence of quantity is to be considered as exerted by b , the abstraction of a being more difficult as the relative quantity of b is increased. On the other hand, if the decomposing force were one acting on b , such as the influence of cohesion, or a divellent affinity exerted to it, the effect of quantity must be considered in relation to a , the abstraction of b being more difficult as the quantity of a is increased.

No law with regard to chemical affinity is more important than that now illustrated, not only from its direct influence, but as modifying the operation of the other circumstances by which chemical action is influenced. The direct corollaries from it may be stated.

First, It follows from it, that the chemical action of any substance on another must diminish as it advances to saturation. Its energy depends on its affinity and quantity; that portion which enters into combination has its affinity saturated, and this being equivalent to its abstraction, the remaining quantity must have a less powerful action. So far as it is not limited by fixed proportions this law operates.

Secondly, A compound subjected to decomposition, must oppose a stronger resistance to the decomposing agent, in proportion as the decomposition proceeds, for the increase in the relative quantity of the one of its ingredients to the other which is abstracted, adds to the force of the attraction between them. Hence, when a substance is separated from a combination by precipitation, it generally retains a portion of the substance with which it was combined. And, in like manner, in decompositions by heat, the decomposition is often only partial, and the last portions of the expelled ingredient are retained with great force.

There is not, however, in every case, this participation. From the interference of cohesion and elasticity, or the predominance of very powerful attractions, decomposition is sometimes rendered complete, and substances are obtained pure and insulated.

Lastly, in decomposing a compound by the action of a body exerting an attraction to one of its constituent parts, the decomposition is often rendered more complete, by adding a larger quantity of the decomposing substance, than is exactly equivalent to the substance abstracted, and the results of chemical action are often materially modified by changes in the proportions. These circumstances frequently demand attention in practical chemistry.

II. COHESION.—Cohesion, or that force by which the particles of the same kind of matter are held together, and from which, when exerted with energy, bodies exist in the solid form, has an influence in counteracting affinity, and opposing chemical action, which has long been observed.

It is evident that a force, which retains the particles of a mass of matter in union, must oppose any action tending to separate them, in order to bring them into new arrangements or combinations, and the ultimate result must depend on the proportion of these to each other. If cohesion is powerful, affinity may be effectually resisted, and no combination take place; and if cohesion be inconsiderable, a weak affinity may be predominant, and a combination be effected. The more powerful aggregation is, the stronger must a chemical attraction be to overcome it, and whatever weakens aggregation must favour combination.

There are, accordingly, a number of examples in chemistry, in which aggregation in bodies is so powerful, that they are not sensibly acted on by others, though combination is effected when the aggregation of the solid

is destroyed. Thus the native oxide of tin resists the action of any acid; it was discovered by Guyton, that this is owing to its strong aggregation, and that when this is overcome by mechanical operations, it becomes soluble. Klaproth found, that the ruby, the sapphire, and the adamantine spar, from the same cause,—the strength of the aggregation between their particles,—are scarcely affected by any chemical agent; but if their cohesion be weakened, they are acted on, and their analysis can be accomplished. Hence the mechanical operations of Trituration, Levigation, and Granulation, are of considerable importance in facilitating chemical action, partly by diminishing aggregation, and partly by increasing the surface at which affinity is exerted.

The observation of the effects of cohesion in counter-acting chemical action, gave rise to the axiom which has long been delivered in chemistry, *Corpora non agunt nisi sint soluta*: Bodies do not act on each other, unless they are dissolved, or in a fluid state. Though to this proposition there are some exceptions, it is generally true. It is seldom that two solid bodies act chemically on each other; while fluids having mutual affinities combine with facility; and fluids act on solids with energy, proportioned to the attractions they have towards them. The fluidity necessary to chemical action is communicated sometimes by the application of heat, sometimes by the addition of a fluid, as water, which dissolves or renders liquid one or both of the bodies concerned, without materially altering the order of their attractions. Hence fusion and solution are the common *media* of chemical action.

It is not true, however, that fluidity is indispensable to chemical action. There are many examples in which two solid bodies, in a state of mechanical division, act chemically on each other. Thus, a number of compound salts, mixed together merely in powder, suffer mutual decompo-

sition : different solid salts too act on ice or snow at low temperatures, at which neither of the ingredients separately can be fluid ; and various earths, when mixed, and exposed to heat, combine and form a fusible compound, at a temperature inferior to what would be requisite to communicate fluidity to either of them. In such cases, the mutual affinity is sufficiently strong to overcome the aggregation in each, and they establish the propriety of the more general expression of the fact,—that to admit of chemical action the attraction of aggregation in bodies must be diminished below the force of the chemical attraction subsisting between them.

When the affinity of a fluid to a solid has overcome the cohesion of the solid, and dissolved as large a portion of it as it can do, it may still dissolve a quantity of a different solid, by the affinity it exerts towards it ; and it sometimes happens, from the reciprocal action of the two solids, that the solution of the second is effected in larger quantity, than it would have been if the other had not been previously dissolved ; and even a fresh portion of the first, if added, will be dissolved. This was observed by Lemery in the solution of nitre and sea-salt in water. Vauquelin found the same phenomenon to be exhibited by a number of saline substances *. Hence the reason that those salts which produce cold during their solution in water, produce it to a greater extent when previously mixed than when they are dissolved separately ; the cold arises from the solution, and a larger quantity of solid matter becomes fluid in a shorter time ; and hence also the difficulty found in many cases of separating completely salts by crystallization which have been dissolved together, as well also as the formation of an uncrystallizable residue †.

* Annales de Chimie, t. xiii. 86.

† Berthollet's Researches, 163.

Cohesion, though weakened in fluids, is not to be regarded as entirely impaired; its existence is evident in the adhesion of the parts of a fluid forming globules, and it is sufficiently powerful to resist the reciprocal action, or to limit the combination of fluids, the mutual affinities of which are weak. In general, however, the resistance it opposes is too inconsiderable to limit the combination, and fluids usually combine in all proportions, especially where there is no considerable difference in specific gravity.

So far the operation of cohesion on chemical action was known to chemists. But, besides these effects, a more extensive influence has been attributed to it by Berthollet, particularly in shewing, that the phenomena referred to certain forces of adhesion, or physical affinity, probably arise from chemical attraction, balanced by the power of cohesion; in illustrating also the cause of the limits to solution, from the decreasing ratio with which attraction is exerted, while the cohesion remains uniform; and in explaining its agency in determining combinations in fixed proportions.

The principal peculiarity in the view which Berthollet gives of the influence of cohesion on chemical action, is, that of regarding it not merely as a quality of bodies actually solid, (or remaining in a small degree in fluids,) resisting the exertion of affinity, and ceasing to act when solidity is destroyed, but as continuing to operate, even when it has been apparently overcome, so that by an increase in its action it may influence chemical combination. Thus, it may be suspended by a superior affinity, or by the agency of heat; and its energy may be so far subdued, as to appear entirely negative; but it still continues so far active, that if these forces are diminished its action will be exerted, even before solidity takes place, and will counteract affinity. Or if, in consequence of new affinities, combinations are produced, it will frequently determine the proportions in which the elements are combined. Being

exerted between the integrant particles resulting from the combination, whenever its intensity is sufficient to counterbalance the affinity of the liquid to the substance formed, it will produce its separation by crystallization or precipitation, will of course withdraw it in part from the sphere of action, and oppose a resistance to any further exertion of chemical power, and by such an operation will fix the proportions. This is the most important effect of cohesion, and I shall have immediately to state this agency of it in considering the causes of the limits of chemical combination.

Farther, from considering cohesion and chemical attraction as antagonist powers, and comparing the effects which arise from them when they are exerted in different degrees of intensity, Berthollet traces various degrees of combination more or less intimate, and thus refers to one principle those varieties of action, which have been considered as produced by peculiar forces, named attraction of adhesion, capillary attraction, physical affinity, and hygrometric affinity. These he regards as mere varieties of chemical attraction, balanced more or less by cohesion. "The distinction attempted to be established by some philosophers between chemical affinity and physical adhesion is without foundation; for the effects which they attribute to the latter, depend on the same cause as those which are owing to affinity, and are only different in the energy of the reciprocal action compared with the resistance opposed to it *."

Thus, if in a solid substance, the cohesion exceed the affinity exerted to it by a liquid, the solid will remain unaltered as to its form or properties, but may still present some shades of union with the liquid. The affinity may indeed be so weak, or the cohesion so strong, that the fluid will even not adhere to the surface of the solid, as in

* Chemical Statics, vol. 1, p. 18.

the example of a drop of water applied to a polished metal; but in other cases this adhesion takes place, and extends along the surface, contrary even to the specific gravity of the liquid, especially where that surface is great, proportioned to the quantity of liquid, as in tubes of narrow diameter, producing the phenomena referred to what is termed Capillary Attraction. From a still stronger affinity, the liquid may be imbibed by the solid, without however the force being sufficiently energetic to separate the particles from their state of cohesion. This happens in hygrometrical phenomena, which were ascribed to this cause by Saussure. If it be a little more powerful, or the cohesion rather less strong, the latter power may be so far weakened by the affinity of the liquid imbibed, that the solid is reduced to powder, as is exemplified in the slacking of lime by water. Sometimes, though not sufficiently powerful to reduce it to its ultimate particles, it is sufficiently so to hold small masses of it suspended for a considerable time, notwithstanding the difference of specific gravity, as is observed in the diffusion of precipitates. And, lastly, if the affinity is still more powerful, and the quantity of fluid sufficiently large, the cohesion is overcome, and the solid is dissolved by the liquid.

In this case a new series of phenomena commences, in which we perceive the relation of cohesion to the former modifying circumstance, quantity of matter. Chemical action is exerted, not only in the ratio of the attraction of one body to another, but likewise in a certain ratio of quantity; hence in solution the power exerted by the liquid, or, rather, the reciprocal tendency to combination in the solid and liquid, diminishes as the solution proceeds. The affinity may at first be sufficiently strong to overcome the cohesion of the solid; but the action of the liquid, in consequence of this law, becoming weaker as it approaches to saturation, it may, after a certain period, be so far re-

duced in force, as to be unable to produce this effect, and the progress of the combination must cease.

We have thus a clear view of the nature of solution, and of the causes which limit it. Formerly the fact was stated as an ultimate one, that a fluid dissolves certain quantities of solids, without the cause of these limits to it being distinctly pointed out. We now perceive it in this relation between cohesion and chemical affinity. When a liquid is poured on a solid, suppose water on a salt, it first overcomes the cohesion of the solid by the attraction it exerts to its particles; hence the solid is dissolved. When the cohesion of the solid can thus be overcome by the affinity of the liquid, why should the solution not proceed until every intermediate consistence between solidity and fluidity is attained? The reason is, that the force of the affinity, in conformity to the law which arises from the effect of quantity, diminishes as there is an approximation to saturation. In the progress of the solution, it arrives, therefore, at an equilibrium with the power of cohesion in the solid, and then, it is obvious, the solution must cease. Hence also the quantity of matter dissolved is increased, by raising the temperature, as this diminishes the force of cohesion.

III. INSOLUBILITY.—The insolubility of a substance in a fluid, which is the medium of chemical action, has an influence on that action similar to that of cohesion, and is indeed nothing but a modification of it in relation to the fluid in which it is exerted. When substances in the liquid state act on each other, their action meets with little foreign resistance, and is therefore, in a great measure, proportional to their affinity and quantity. But if one of them be solid, and be also insoluble in the fluid which is the medium of action, the insoluble matter must present comparatively few points of contact; it is withdrawn from the sphere of action; and if it be opposed to a combina-

tion, it can act with comparatively little energy. From the same cause, if it be a compound, and be acted on by any substance tending to combine with one of its principles, its insolubility must in some measure protect it, as abstracting it from the action of the decomposing substance.

Insolubility may also determine the proportions in which a compound is formed ; for if, in the progress of combination, a compound be produced which is insoluble, it will be immediately precipitated, become insulated, and thus fixed in its proportions.

Lastly, it admits of decomposition being more complete. If the substance eliminated in the progress of chemical decomposition be soluble, as it remains within the sphere of action, it continues to oppose the action of the decomposing substance, and the body to which each has an attraction is shared between them according to their affinities and quantities. But if it be insoluble, being withdrawn, it opposes no obstacle to the progress of the decomposition, which is therefore more rapid and complete.

IV. SPECIFIC GRAVITY.—Great specific gravity in a substance having much cohesion, or of sparing solubility, must co-operate with these qualities in influencing chemical action. It withdraws the body possessed of it from the sphere of action, and the subsidence can be but imperfectly counteracted by agitation : hence it must so far retard its combinations ; it must also diminish its power in effecting decomposition ; and it must, if the substance be a compound, resist its decomposition from the action of other bodies upon it.

V. ELASTICITY.—This property is possessed in such a degree as to produce sensible chemical effects, only by æriform substances. Though the reverse of cohesion, it operates on a similar principle, or influences chemical action, by withdrawing the particles from the sphere of at-

traction. According to its various degrees of energy, and according as it is modified by other circumstances, it resists combination, or favours decomposition.

When two elastic fluids are mingled together, though they have mutual affinities, they do not in the greater number of cases combine. *A priori*, we might be led to expect that they would combine with rapidity; for as cohesion is a force counteracting affinity, and as in the elastic or æriform fluids it is subverted, any attraction existing between these bodies, it might be supposed, would be exerted with effect. We find this, however, seldom the case; and between a number of elastic fluids, intimate combination is not easily established.

This is to be ascribed to their elasticity. A substance in the ærial form consists of particles placed at great distances, and repelling each other. When two airs, therefore, are mingled together, their particles are without the sphere of chemical attraction; their mutual affinity is feebly exerted, and they cannot be combined, but by subjecting them to circumstances in which this obstacle is lessened or removed.

In conformity to this view, it is found, that, in vapours, the facility of combination is greater than in the permanent airs or gases; there is a tendency in the former to condensation and approximation of their particles; they are on the verge as it were of fluidity; hence they are under circumstances favourable to their mutual action. When the affinity too is very energetic in the permanent gases, it is capable of overcoming the obstacle from elasticity, and of uniting their particles, as in the example of the acid gases presented to ammonia. And even in those airs, which, when mixed together, do not combine intimately, a combination may be effected, if pressure be applied to a sufficient extent. This has been established by the experiments of Mr Northmore, in which, by the operation of

condensation, various elastic fluids were combined *, and by an experiment of Biot, in which, by the same operation quickly applied in a condensing syringe, oxygen and hydrogen gases are made to combine, with the sudden extrication of heat and light †. On the same principle rarefaction has the opposite effect, that of preventing the combination of elastic fluids. This appeared to be established by certain experiments by Grotthus, in which mixtures of different inflammable elastic fluids with oxygen gas entered less readily into combination, so as to suffer combustion when rarefied, either by the abstraction of pressure or by heat, than when in a denser state. And even solid combustible substances, such as phosphorus, burned with difficulty in a rarefied atmosphere, and with increased facility in a dense atmosphere ‡. Sir H. Davy confirmed these results, so far as that combustion is impeded by rarefaction from abstraction of pressure; but he finds it to be the reverse with regard to rarefaction produced by heat; and he infers, that the diminished effect in the former case is to be ascribed not directly to the state of rarity, but to this not admitting of the evolution of sufficient heat to support combustion. In conformity to this view he supposes that condensation of a mixture of elastic fluids favours their combination merely by augmenting the temperature §. This subject is to be afterwards considered, in considering the relation of temperature to combustion: at present it is sufficient to remark, that it seems almost necessarily to follow, that elasticity, by placing the particles of bodies at greater distances, must counteract the exertion of their mutual attraction; and it is difficult to conceive of heat favouring combination in any other mode than by modifying the external forces of elasticity and cohesion.

* Nicholson's Journal, vol. xii. and xiii.

† Ibid. vol. xiii, p. 213. ‡ Ibid. vol. xxxv.

§ Philosophical Transactions, 1817.

From the same operation of elasticity a combination may be more easily effected between a liquid and an air, than between two airs, since its absence in the one so far removes the obstacle to the exertion of their mutual attraction. Hence, too, condensation promotes the combination of elastic fluids with liquids. The quantity of an aëriform fluid absorbed by water or any other liquid, is greater, if strong compression is applied, than if it is not; and by a compression sufficiently powerful, very large quantities of airs, which otherwise are sparingly absorbed by the liquid, may be combined with it, and remain combined as long as the compression is applied.

By a similar operation combinations of this kind are promoted by cold. At a low temperature, more of the air is absorbed by the water than at a high temperature, because by the cold its elasticity is repressed. This, however, has its limits; for if the degree of cold be so great as to increase materially the cohesion of the liquid, this may more than counterbalance the advantage gained by the diminution of elasticity in the air, and may place bounds to the combination; and in freezing a liquid which has been combined with an air, it generally happens, from this cause, that in the moment of freezing the air is expelled. Hence, too, heat often favours the combination of aëriform fluids with solid substances; for although the application of heat increases the elasticity of the one, and so far is unfavourable to the combination, it diminishes the cohesion of the other, and this may exceed the opposite effect, and enable the bodies to combine. In such cases it generally happens, that by raising the heat higher, the combination is subverted, and the elastic ingredient expelled.

From these facts it follows, that elasticity is to be regarded as a force opposed to the exertion of chemical attraction. It may be remarked, however, that although the elasticity of aërial fluids is a cause opposing their intimate

combination, their mutual affinity appears in general to be so far exerted, that when they are mingled it counteracts their specific gravity, and prevents them from separating from each other. The action is not sufficiently energetic to overcome the elasticity of each, and hence it is not attended by any change of volume, any evolution or absorption of heat, or the production of any new property, but merely retains them in a state of uniform diffusion. If, however, by any arrangement, their particles are farther approximated, their affinity is exerted with more energy, and an intimate combination is formed.

We have still to consider elasticity as it favours decomposition.

If a compound consist of a solid substance, and of another, which, when uncombined, acquires elasticity, or exists in the *aëriform* state, it will be more easy of decomposition, either by the application of heat, or by the intervention of superior affinity, than if it consisted of two non-elastic bodies.

If it be exposed to heat, it will be unequally acted on: the elasticity of the one ingredient will be favoured, and this to a greater extent as the temperature is raised, until at length it is able to counteract the affinity between the ingredients; they will then be separated from each other, and the greater part of the one that is elastic expelled. A portion may indeed be retained, from the affinity of the solid being increased, by the increase in its relative quantity by the progress of the decomposition; but this will be comparatively small.

The same cause operates, in favouring decomposition by the exertion of a superior chemical affinity. If, to a compound composed of an *aëriform*, and a solid or liquid body, a substance be added which has an attraction to the solid ingredient, it combines with it, and excludes a portion of the air that was in combination. If this were to remain within the sphere of action, it would oppose a resistance

to the progress of the decomposition, by the attraction it continued to exert to the substance with which it had been combined, counteracting that of the decomposing substance. But being entirely withdrawn by its transition into the elastic form, this ceases. Hence the decomposition of compounds of this kind;—those consisting of a solid or liquid combined with an air, is more complete than the decomposition of compounds consisting of inelastic ingredients. Such decompositions also are much favoured by the application of heat, which, increasing the elasticity of the volatile substance, favours the affinity of the more fixed, and frequently causes it to predominate though in itself weaker than the affinity of the elastic ingredient to the base of the combination.

VI. EFFLORESCENCE.—The effect of this property on chemical action, is comparatively trivial and limited. Scheele had observed, that in several saline mixtures, made into the consistence of a paste, decompositions were produced, and that one of the compounds, resulting from the decomposition, rose gradually through the mass, and formed an efflorescence on its surface. Berthollet supposes, apparently with reason, that its being thus withdrawn from the sphere of action, contributes to the progress of the decomposition, or allows it to proceed farther than it would otherwise do. The case in which it has been principally observed, is in the decomposition of sea-salt by lime, or by iron, noticed by Scheele; and Berthollet applied the observation to the explanation of the production of mineral alkali or soda, in the beds of lakes in Egypt. It serves to explain the appearance of the same substance on walls covered with mortar, and perhaps it may be applied with advantage in practical chemistry. The circumstances which appear to favour it are, a porous mass, a certain degree of humidity, and a disposition to crystallize in the efflorescent substance.

VII TEMPERATURE.—Temperature denotes the state of bodies with regard to heat and cold. Much of its effect on chemical action is to be ascribed to its influence as connected with the changes it produces on the cohesion, and the elasticity of bodies. Its effect, however, is usually compounded of the two, or arises from the changes produced on both of them at the same time. On this account it requires a separate statement ; and this also is demanded by the importance of the subject.

In general, heat favours combination. Bodies, which, at a low temperature, do not act on each other, combine when their temperature is raised ; and with regard to many substances, it requires to be raised to considerable intensity, to effect their combination.

When they are melted by the heat, it is easy to perceive to what cause its influence is to be ascribed ; it overcomes the cohesion of the fused substance, and thus removes an obstacle to the exertion of affinity. But there are many cases in which, without fusing bodies, heat favours their combination ; as in the solutions of salts in water, in the mutual action of earths, the combinations of metals with oxygen, and many others. In these, it is still to be regarded as operating, by lessening the cohesion of the solid matter. Every degree of heat communicated to a solid substance weakens its cohesion, though it may not be capable of overcoming it to that extent, as to cause it to pass into the fluid form ; and this diminution of cohesion may so far remove the obstacle to combination, that if a powerful affinity exist between the bodies, it may be exerted with effect.

The power of heat, however, in thus favouring combination, by diminishing cohesion, is frequently counteracted by its increasing elasticity. If an elastic fluid is to be combined with a solid, the obstacles to the exertion of their mutual attraction are the cohesion of the one and the elasticity of the other. Heat will diminish the former, but it

will also augment the latter; and so far as the one effect would favour combination, the other opposes it. Hence, if the affinity existing between these substances is not strong, it may not be possible to effect their combination by raising their temperature, as in exposing, for example, gold or silver to oxygen gas. Or if at one degree of temperature they have combined together, the exposing the compound to a higher temperature may separate them, as is the case with quicksilver and oxygen. Hence also, if the cohesion is lessened by other means, the combination may be effected at a moderate temperature, as we observe in the facility with which metallic alloys, and especially alloys of the metals with quicksilver, combine with oxygen, compared with the same metals in their pure state.

Even the same operation may influence the action of inelastic substances. If the action of a fluid on a solid be aided by heat, the whole effect arising from the diminution of cohesion in the solid may not be obtained, as it may be counteracted from the expansion produced in the fluid; and if the fluid be highly expansible or volatile, this may weaken considerably the energy of its affinity.

To the operation of heat on cohesion and elasticity, now described, are to be attributed the differences of affinity between the same substance, when exerted in the humid way or by the medium of solution, and in the dry way or by exposure to heat. In the former, cohesion is counteracted, while the elasticity of any of the ingredients is not affected; in the latter, if the one power is diminished, the other is augmented, and this is frequently sufficient to change the results. Bergman pointed out this operation of heat on elasticity, as modifying the affinities exerted under these different circumstances*.

A high temperature is equally powerful in favouring

* Dissertation on Elective Attractions, p. 15.

chemical decomposition. Many substances remain in union within a considerable range of temperature ; but if heated beyond a certain point, their mutual attraction is weakened, they separate, and the compound is decomposed. Such decompositions take place generally, perhaps always, in those compounds, one of the ingredients of which exists when uncombined in the aëriform state. Hence the operation of heat in occasioning them is evidently owing to its favouring the elasticity of this ingredient, acting on it with greater effect than on the other, and by the distance at which it places the particles overcoming attraction.

In some cases of decomposition favoured by heat, the attraction of a third body is introduced ; but the explanation of the agency of the high temperature is still the same. By adding to the elasticity of the more volatile ingredient, it weakens its affinity, and hence favours the combination of the two substances which are more fixed. On the same principle, heat often promotes the mutual decomposition of two compounds mixed together,—favouring the union of the two more volatile ingredients, and thus allowing an attraction to be exerted with less resistance between the others.

In all cases, therefore, in which heat favours chemical action, it does so by the change it occasions in the cohesion or in the elasticity of bodies ; but the one of these frequently modifies the effect which would result from the other, and thus this power often apparently produces opposite effects. In a certain degree it may favour combination, and in a still higher degree it may occasion the separation of the very substances it had enabled to combine ; and it is only by considering these effects in their different relations, that we obtain a just theory of its operation.

The same view is to be taken of the operation of a low temperature or of cold on chemical action. By diminish-

ing elasticity, it frequently favours combinations; and in other cases, by increasing cohesion, it may counteract this, or may subvert existing affinities, and give rise to decompositions. And it may often happen, that both qualities may be affected, and produce results, which, if this were not attended to, would not be expected. By a low temperature, we may thus promote the combination of an æriform body with a liquid; but if we reduce the temperature too low, that is, near to the point at which the liquid congeals, the additional force given to cohesion may counteract the effect arising from the diminution of elasticity, and may impede the combination. Or if the temperature be reduced so low as to freeze the fluid, an æriform body held in solution by it may be expelled, owing to the cohesion acquired by the congelation.

There is a peculiar case in which combination is promoted by heat, where the result is different from what would be expected;—that of elastic fluids which have a mutual attraction, but do not combine at a common temperature. Two airs, having such an attraction, may be mingled together without entering into intimate combination, owing to the repulsion between the particles of each, so that they are placed beyond the sphere of chemical action. But on applying a temperature equal to ignition, as by introducing an ignited spark, or an electrical discharge, the particles, in some cases through the whole mixture, are instantly united; in other cases, a stream of sparks requires to be kept up, but in these also the combination, though proceeding more slowly, is complete. Yet, in conformity to the cause assigned for their not combining, it apparently follows, that the application of heat, by increasing the elasticity, and augmenting the distances between the particles, must counteract instead of facilitating the combination. How therefore is the fact to be reconciled with the theory?

I have given the following explanation of this singular

circumstance. When a spark is introduced into the mixture of two gases having an attraction to each other, the point on which it falls is heated to an intense degree; whence an expansion, proceeding from that point as from a centre, is produced; and this expansion, by the pressure it must occasion on the surrounding particles, will cause them to approximate, and thus to unite. The whole effect is instantaneous, and it is upon the sudden operation that it depends. Were the heat to be progressively raised, the expansion would be extended over the whole mass, and would be equal throughout; the particles, therefore, if proportional pressure were not applied, would be farther separated. But a small portion being merely heated to a high degree, while the surrounding particles remain at their usual temperature, the expansion from the former must press upon the latter, much more quickly than the temperature can be communicated: hence the approximation within the verge of chemical attraction, and the union that takes place. When it is effected, more caloric is rapidly, but successively, extricated by the combination itself, which will produce a similar effect on the remaining mass, till the combination is completed. There are some gases, however, from the union of which so little heat is extricated, that the introduction of a single spark is insufficient, and therefore a stream of sparks must be kept up.

The same explanation has been given by Berthollet *. It is confirmed by the experiment by Biot, already referred to, that of producing, by mechanical compression suddenly applied, the combination of two aerial bodies which at moderate temperatures do not otherwise combine, the combination being accompanied with phenomena similar to those which appear when they are united by

* Chemical Statics, vol. i, p. 232.

an ignited spark. It has been called in question by Sir H. Davy, who considers the effect as depending directly on the increased temperature produced by the spark, and not on compression,—and in conformity to this, as has been already remarked, (page 99.) he considers the *heat* produced by the compression of gases as the direct cause of their combination. But the difficulty remains, how heat should favour combination, except in so far as it affects the state of cohesion or elasticity, or produces approximation of the particles of an elastic fluid by local compression: no other obvious operation arising from it can be assigned.

The circumstances now enumerated, not only influence the exertion of chemical attraction as to its force, but also as to its rapidity. Where the cohesion of a body is great, it will be more slowly acted on by a fluid than if the cohesion were less considerable: hence the utility of those operations which diminish aggregation, in promoting chemical action. It is obvious, also, that chemical action must be slower when resulting from a weak than when arising from an energetic attraction; and, for the same reason, as the force of attraction diminishes as bodies approach to saturation, a chemical action, which at its commencement may be rapid, must in its progress become more slow. Agitation hastens the chemical action of a solid or a liquid, by removing from the surface of the solid the portion of liquid already saturated with it, and which, from its greater specific gravity, would otherwise remain covering it, and protecting it from the action of the rest of the liquid. And, on a similar principle, agitation accelerates the combination of an æriform body with a liquid, renewing the surface, and distributing with uniformity the combination over the whole mass. Lastly, a high temperature renders chemical action more rapid, by

diminishing or removing those circumstances by which affinity is counteracted.

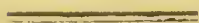
It is often necessary to attend to the slowness of chemical action to avoid erroneous conclusions ; substances which, when mixed together, give no indication of mutual action, acting and producing even complete changes when sufficient time is allowed.

An important corollary flows from the consideration of the influence of the preceding circumstances on the exertion of chemical attraction,—that in no case can it be affirmed, that bodies have no attraction to each other. There are substances which we cannot combine together, as oil and water, water and quicksilver, &c.; and from such facts, it was regarded as a law, that between some bodies no chemical attraction exists. The fallacy of this conclusion is obvious from the consideration, that combination is not the simple result of the exertion of attraction, but of attraction prevailing over cohesion, elasticity, or difference of specific gravity ; and therefore it may be incapable of being effected, as much from the predominance of these forces, as from the absence of reciprocal attraction. Ardent spirit dissolves no sensible portion of sea salt ; but this may arise from the affinity which the spirit does exert to the salt, not being sufficiently strong to overcome its cohesion and specific gravity ; and we cannot employ heat to lessen these opposing qualities with effect, because the spirit is so expansible, and so much disposed to volatility, that as much power would be lost on the one hand, as would be gained on the other. A similar explanation applies where two liquids cannot be combined together ; for although in bodies in this state cohesion is weakened, it still exists, and may be sufficient to counteract a weak affinity. Thus it in some cases places limits to combination, as in the example of sulphuric ether and water, the former of which combines

with the latter only in the proportion of one-tenth; and it may in other cases, where the affinity is still weaker, as is probably the case in that of oil and water, be able, with the difference of specific gravity, to resist attraction, and prevent any combination. In the case of a solid and aëri-form substance, the obstacles to combination are still more powerful, being the cohesion of the one, and the elasticity of the other, and the circumstance which will diminish the former, that is, a high temperature, will augment the latter. Hence we may expect in this kind of relation more frequent examples of substances refusing to combine, but evidently without the conclusion following, that these substances have no mutual attraction. Lastly, in elastic fluids, the elasticity may frequently counteract a weak affinity, even under the circumstances by which their mutual action is promoted.

If this reasoning required any illustration, it might receive it, from taking examples of substances which are combined with difficulty, and supposing either their affinity to have been a little weaker than it is, or the counteracting circumstances somewhat more powerful. Thus gold is combined with difficulty with oxygen, and only in indirect modes. It is obvious, that if the affinity between them had been a little weaker, or the cohesion of the gold rather greater than it is, even these would have failed: and the erroneous conclusion might have been drawn, that these substances had no mutual attraction.

It is difficult to conceive of attraction than as a force possessed by every particle of matter and exerted to every other; and the theory is evidently superior, which supposes its exertion to be prevented from being effective, by the interference of extraneous forces, to that which supposes, that between certain substances it is wanting, especially since in all cases the action of such forces can be demonstrated to a certain extent, which may be sufficient to account for the results.



From the conclusion, that all bodies have probably mutual affinities, combined with the consideration of the important influence of cohesion, elasticity, and other circumstances, on the exertion of chemical attraction, another inference follows as extremely probable,—that the affinities exerted by compounds may be the affinities of their constituent principles, modified by the conditions under which they exist in the combination. The affinities of a compound are generally indeed totally dissimilar to those of its elements: it combines with substances to which they shew no attraction, and it refuses to unite with others with which they form intimate combinations: the difference indeed is so great, that it must have been difficult to conceive how they could arise from any modification of the elementary affinities. The notion, therefore, was adopted, that when two substances combine together, they form by their union the integrant particle of the compound:—that the attractions it exerts to other bodies are exerted not from its ultimate elements, but from these integrant particles, and arise rather from their magnitude, configuration, or other qualities, than from any modification of their elementary parts:—that when water, for example, exerts attractions, these are from the particles of the water as such, and not from the ingredients of which it is composed. It has also been supposed, that between these integrant particles of a compound, the cohesive attraction is exerted which gives it its peculiar form. This, however, is rather an hypothesis, by which the chemical actions exerted by a compound as such, are represented with more facility. From the consideration of the important influence of saturation, cohesion, and other circumstances on affinity, the opinion may be maintained, that the attractions of compounds are the modified attrac-

tions of their constituent principles ; and Berthollet has shewn, with much ingenuity, how the circumstances known to exist in combinations may, from their acknowledged influence on chemical affinity, account for the differences between the attractions of compounds and those of their elements.

Thus, from the affinity which one of the elements of a compound exerts to the other, the affinities of either to other substances must be so far counteracted, and hence the cause of what is generally the case, that the attractions exerted by a compound are less numerous and less powerful than those of its constituent parts, and that the ultimate products of successive combinations are usually substances having little energy of chemical action. But this is modified by other circumstances attending the combination, which may either concur with it, and still farther diminish their force, or which may counteract it, and render them more energetic.

The action, for example, of a substance, depends not only on the energy of its affinity, but also on the quantity of it within the sphere of action. If an aëriform body, therefore, is condensed in a combination so as to exist in the liquid state, it derives from the combination the advantages of acting in a larger mass, and of the removal also of the obstacle of elasticity, circumstances which may render its affinities both more powerful and more extensive in their action. It is true, that this is counteracted by the diminution in the strength of its affinity, from the saturation under which it exists in the combination ; but still this may not be equal, or may be even inferior to the augmentation of energy acquired by the condensation. Potash, by any attraction which it may exert to oxygen, or to nitrogen, may be unable to overcome their elasticity ; but when they are condensed in a combined state in nitric acid, it unites with them, in other words, with this acid, with rapidity. To this perhaps is to be ascribed the general

energy in the action of acids ; probably also, the almost universal agency of water.

In like manner, if a substance by combination pass from the solid to the liquid state, it acquires the advantages in facility of action from liquidity ; and its affinities, formerly counteracted by its cohesion, may now, notwithstanding its combination, be exerted with more effect. Sulphur, at a common temperature, does not combine with oxygen gas, but when united with potash, so as to be soluble in water, the solution condenses oxygen easily, which may be ascribed principally to the fluidity of the sulphur at this temperature, aided by the affinity exerted by the potash to the oxygen.

On the other hand, if the result of a combination is the transition of a substance into the solid state, the cohesion acquired may add to the diminution in the strength of its affinities from saturation. Potash and nitric acid are separately soluble in alkohol, but the compound they form, nitrate of potash, is insoluble ; owing, according to this view, partly to its cohesion, and partly to the diminution in the force of the affinities of its elements, by their mutual saturation. It is still soluble however in water, as its constituent principles are more soluble in that fluid than in alkohol. The transition to the elastic form, by combination, may, in like manner, concur with the effect of saturation, in diminishing the energy of action of the body suffering this change.

We thus perceive how, supposing the affinities of substances to remain in their combinations, they may be so far modified, as to be different from what they were in their insulated state ; and we perceive, therefore, that the affinities of compounds may be the modified affinities of their constituent elements. Admitting this, however, these modified affinities should be regarded as a single and integral force, operating as such, while the body remains undecomposed ; and we may speak with equal propriety of the at-

tractions of a compound, as of the attractions of a simple substance. We thus, too, avoid any ambiguity which may arise from the application of the theory to the explanation of chemical phenomena, should it even be not fully established. And that there does exist even a real distinction with regard to this, is apparent from the fact, that there are combinations of a compound body to an additional portion of one of its ingredients, which appear to be different in some respects, particularly in energy and permanence, from the kind of combination that would be formed by the direct union of the elements of the compound in a different proportion.

The affinities exerted by a compound, thus arising from the modified affinities of its constituent principles, were named by Berthollet *RESULTING*, in opposition to the individual affinities belonging to these principles, which he names *ELEMENTARY*. Water being a compound body, the affinities it exerts as such may be named *resulting*, though the elementary affinities of its elements may also be sometimes exerted. As chemical action is reciprocal, Berthollet gives likewise the name of *resulting affinity* to the attraction which a simple substance exerts to a compound, when it does not change the composition of the compound. Thus a substance exerting an attraction to one of the principles of water, exerts an elementary affinity; when it exerts attractions to both, in other words to the water itself, the affinity is *resulting*.

The following general principles are connected with this theory of *Resulting Affinity*. If the attraction of a substance to one of the principles of a compound be much superior to its attraction to the other, an elementary affinity will be called into action, and the compound will be decomposed. If the attraction exerted be nearly equal to each, a *resulting affinity* will be established, and the substance exerting it will combine with the compound; and this will even happen where there is an inequality, if it is

not very great, as the affinity exerted by the one of these principles to the other is a force the effect of which is to maintain the combination, to counteract therefore the elementary, and favour the resulting affinity. Lastly, when an elementary affinity is exerted at first, as it must become weaker in the approach to saturation, it will at length not exceed in force the affinity exerted to the other principle of the compound, an equilibrium will be established, and the action will terminate in the exertion of a resulting affinity. The application of these principles affords some happy explanations of more minute chemical phenomena, of which a few examples are given in the note beneath*.

An important application of this doctrine is to be found in the explanation it affords of certain anomalous cases of

* Water, in dissolving a neutral salt, acts by a resulting affinity, or by the astractions it exerts to the principles of the salt, modified by the attractions they exert to each other. But if its attraction to one of these principles be much superior to what it is to the other, especially where the affinity between them is not very strong, the affinity it exerts is elementary, and the salt is decomposed. This is exemplified in a number of the metallic salts, in which water abstracts their acid.

Sulphuric acid is a compound of oxygen and sulphur, and, in combining with potash, is supposed to act by an affinity which results from the affinities of these elements. The reciprocal action of potash is also composed of its affinities to the principles which constitute sulphuric acid. Both therefore are resulting; and when exerted, they effect the combination of the acid and potash. But the elementary affinities of sulphuric acid may also be exerted. Thus, when heated on a metal, the metal does not exert an attraction to the entire acid, but to its oxygen. This is therefore an elementary affinity; but in the progress of the action, the attraction of the metal to an additional portion of oxygen becoming nearly equal to its attraction to sulphur, at least when that attraction is aided by the attraction of the oxygen to sulphur, it exerts an affinity to

chemical action, which have been classed together, under the name of Disposing Affinity. These are of a very peculiar kind. In a number of cases, two bodies are found incapable of combining; but the circumstances still remaining the same, their combination is effected by the addition of a third body, though it has no apparent attraction to either of the others; or at least none which, by any obvious operation, can facilitate their union. It has been observed, indeed, that the substance which thus predisposes to the combination, has an attraction to the compound formed by the combination of the others, and to this attraction its agency has been ascribed,—an opinion which appears very absurd, since the attraction which it might exert to a substance if it were formed, cannot be a cause of the formation of that substance. If, however, the affinities of a compound are the modified affinities of its elements, it may receive an explanation.

Water, for example, is a compound of oxygen and hy-

the entire acid, with which therefore the oxidated metal now combines. In this case, the elementary pass into resulting affinities. This, in conformity to these principles, affords a refined view of the theory of the action of acids on metals. Metals may be conceived to have an attraction both to the oxygen of an acid and to its base, but stronger to the former than to the latter. When submitted therefore to the action of an acid, the metal first attracts a portion of oxygen, but its affinity to this principle diminishing as it approaches to saturation, comes at length not to be greater than its attraction to the base of the acid, and then the entire acid enters into the combination. Hence the law observed, in metallic solutions, that a metal must be oxidated before it combines with an acid. If its affinity to oxygen is too weak to decompose the acid, being still weaker to the base, it cannot exert a resulting affinity; but if previously oxidated, this bringing its affinity to the base to an equality with the affinity it has to oxygen, it combines with the entire acid.

drogen. Iron has an affinity to oxygen, but not sufficiently strong to decompose water with celerity at a common temperature. But if a little sulphuric acid be added, the decomposition of the water by the iron commences, and proceeds rapidly, the iron receives oxygen, forming oxide of iron, and the compound thus formed combines with the acid. In this case the acid is said to operate by a disposing affinity. Now, the rationale of this, according to the preceding principles, may be pointed out. If the affinity which sulphuric acid exerts to oxide of iron be the modified affinities of it to the two elements, iron and oxygen, these may be exerted by the acid to these elements previous to their combination, and concurring with the affinity which they mutually exert, may produce a union of forces, whence their combination is established, and by which of course the water is decomposed. Again, sulphur does not combine with oxygen at natural temperatures, but if it be united with lime, the compound, when dissolved in water, absorbs oxygen with rapidity. The lime therefore in this case is said to exert a disposing affinity, and the effect, according to the explanation once given, depends on its attraction to the sulphuric acid, the compound produced by the union of the sulphur with oxygen. This appeared absurd. But if the affinity of sulphuric acid to lime be the modified affinities of its elements, these may be exerted even in their elementary state, and aid so far the affinities which these elements exert to each other, as to effect the union of the sulphur, oxygen, and lime. All the cases of disposing affinity are probably thus examples of the concurrence of affinities which singly are not effective, and frequently even not apparent.

SECT. IV.—*Of the Limits to the Exertion of Chemical Attraction.*

CHEMICAL ATTRACTION obeys certain limits; first, with regard to the different proportions or relative quantities in which it causes bodies to combine; and, secondly, with regard to the number of substances between which it may be exerted, so as to bring them into simultaneous combination. These form two subjects distinct from each other, but both comprised under the title of the present section.

I. Of the limits to attraction with regard to the relative quantities in which bodies may be combined.

The facts on this subject I have arranged under the following general propositions.

1st, There are cases in which there is no limitation with regard to proportions,—two bodies combining together with equal facility in whatever relative quantity the one may be present to the other. This occurs chiefly in the combination of bodies in the liquid form, and where the compound remains liquid: the combination of pure ardent spirit, or alcohol, with water, or of sulphuric acid or nitric acid with water, affords an example of it. And that a real combination takes place in every proportion, is proved by the facts, that the two bodies, though of different specific gravities, do not separate from each other, and in all proportions the compound formed has a specific gravity different from the mean specific gravities of the bodies combined. The same result is observed in the combination of some solids, particularly of a number of the metals with each other.

2d, There is a variety of combination exemplified by a number of bodies, in which it is unlimited to a certain proportion, but at this it ceases, and no farther quantity of one of the bodies can be combined with the other.

This is illustrated in the solution of a salt in water. Any quantity of the salt, up to a certain quantity of it, may be combined with the water with equal facility; but after a certain portion is added, the combination ceases to proceed, the mutual attraction is no longer exerted with effect, and if any more salt be added it remains undissolved. The limitation to the combination in this case is named Saturation, and when the water has dissolved the largest quantity of the salt which it can dissolve, it is said to be saturated with it.

3d, Combination is in some cases so strictly limited, that it takes place only in one proportion: in whatever other relative quantities two bodies may be presented to each other, they unite in this precise proportion, and any excess either of the one or of the other remains uncombined. Water affords an example of a combination of this kind; its constituent elements are combined in a proportion perfectly determinate, that of 87.5 by weight of the one, to 12.5 of the other, and they can be united in no other proportion than this.

Lastly, Attraction is exerted between many bodies in such a manner that they may be combined in two, three, or four different proportions, but each of these is perfectly determinate, and they are capable of combining in no proportions different from these. Sulphur and oxygen combine in the proportion of 50 of the one to 50 of the other: they also combine in the proportion of 40 of sulphur and 60 of oxygen. But they cannot be combined in any other proportions; and if presented to each other in different quantities, and placed under the circumstances which are favourable to the exertion of chemical attraction, they always unite in one or other of these proportions. There are many similar examples. It is chiefly where attraction is exerted between bodies with much strength, that combinations in definite proportions are established, and that the peculiar laws regulating these

are observed. Where weaker attractions operate, combination is either unlimited with regard to proportions, the difference at any particular proportion being so inconsiderable as not to insulate the combination at this; or if limited, the limits arise from the operation of external forces.

The compounds formed by these combinations of the same principles in different proportions, differ always in their properties from each other, and frequently the differences are as great as between compounds formed of principles altogether dissimilar. Nearly all the varieties of properties among the substances belonging to the vegetable and to the animal kingdom are owing to this cause. They consist of the same elements; some diversity may arise from the mode of combination, but more is to be ascribed to the very different proportions in which they are combined.

When combination takes place in these determinate proportions, it often happens that in one proportion the properties of the bodies combined are mutually neutralized; that is, the compound retains the more distinctive properties of neither of its component parts, while in other proportions the properties of the one which is in excess may be recognised, weakened perhaps, but still existing to a certain extent. The particular stage of the combination at which this happens is termed the point of Neutralization, or sometimes the point of Saturation. This term of saturation, however, is more frequently applied, as has been stated above, to denote the extreme of combination, or the state in which a body retains the largest quantity of another body with which it can combine; and these two states do not always coincide, but are often the reverse. It is proper therefore to distinguish them. In many combinations, this result with regard to neutralization, as opposed to any different result, does not occur;

the properties of the substances combining are equally lost in all the proportions in which they unite.

When combination is established between two bodies apparently in different proportions, it has been supposed, in some cases at least, that one combination of them only exists, but that the compound thus formed unites with an additional proportion of either of the constituent elements. An acid and an alkaline base, for example, may combine in one specific proportion in which they are mutually neutralized, and they may also form a compound in which there is an excess either of the one ingredient or of the other. But instead of supposing, that in this the whole quantities are in direct combination, it is supposed that the requisite proportions are combined to form the neutral compound, and that to this the additional proportion of either is added. In some cases of loose combination this appears to be the case, but there appears to be no foundation for the assumption with regard to more intimate combinations.

When attraction is exerted between two bodies in different proportions, it is with different degrees of strength in each; so that taking one body in a certain fixed quantity, and considering the other as united with it in different proportions, the latter, in the first or smallest proportion in which it is combined with the other, is retained with more force in opposition to any decomposing agency tending to abstract it, than it is in the second proportion, and in the second is retained with more force than in the third. This general fact, which has been expressed by saying, that attraction is in the inverse ratio to saturation, has been already illustrated, as falling under the law with regard to the influence of quantity on chemical affinity. The combinations of oxygen and nitrogen afford an example of it. Considering the nitrogen as the fixed substance, the compound most easily decomposed by any force abstracting the oxygen, is that in which

the proportion of the latter is largest ; and its decomposition is in general only partial, that is, so much oxygen only is abstracted that it passes into the second combination : this, when subjected to a decomposing force, is in like manner subject to partial decomposition, so much oxygen being abstracted as converts it into the first ; and it requires a decomposing agency still more powerful to subvert this, and leave the nitrogen pure.

I have next to state a very important general fact or law connected with these combinations, in which definite proportions are established. It was first brought distinctly into view as connected with a system of chemical combination proposed by Mr Dalton, and was nearly about the same time more directly inferred by Dr Wollaston from experimental investigation.

All bodies consist of atoms, or particles extremely minute, between which chemical attraction is exerted. It is conceivable that when two bodies combine together, the mutual attraction may be exerted from a certain number of particles of the one, to a certain number of particles of the other : or, instead of this, it is possible that one particle of the one body may combine with one particle of the other, with two, with three, or with four particles. It is this latter supposition which Mr Dalton maintained. Bodies combine, he supposed, atom with atom individually ; and when two bodies combine in different proportions, the combinations are supposed to be first one atom of the one with one of the other ;—then one atom with two, &c. as expressed in the following table.

1 atom of A + 1 atom of B = 1 atom of C, binary.

1 atom of A + 2 atoms of B = 1 atom of D, ternary.

2 atoms of A + 1 atom of B = 1 atom of E, ternary.

1 atom of A + 3 atoms of B = 1 atom of F, quaternary.

3 atoms of A + 1 atom of B = 1 atom of G, quaternary, &c.

“ When only one combination of two bodies can be obtained, it must be presumed to be a binary one, unless some cause appear to the contrary; when two combinations are observed, they must be presumed to be a binary and a ternary; when three combinations are obtained, we may expect one to be a binary, and the other two ternary: when four combinations are observed, we should expect one binary, two ternary, and one quaternary,” &c. *.

Now, in this view of chemical combination is implied the important law, that in the combinations of two bodies in different proportions, a simple arithmetical relation will exist between these proportions, so that the larger quantity of one ingredient is expressed by some simple multiple of the smaller quantity, in which it unites with the other. Considering the one body as the base, and in a fixed quantity, that is, taking it as unity, and considering the first or lowest proportion of the other as 1, the second proportion will be 2, the third 3, the fourth 4, and so on in the same ratio, according to the number of combinations. Or suppose 100 parts of A to combine in the first proportion with 7 of B, in the second proportion 100 of A will combine with 14 of B, in the third 100 with 21, and in the fourth 100 with 28.

The same law had been inferred by Dr Wollaston from direct experimental results. Acids combine with alkaline bases in different proportions; in one proportion the properties of the two bodies are neutralized; in other proportions there is an excess of acid, or an excess of base, retaining its characteristic properties to a certain extent. Dr Wollaston found that this excess of either bore a certain arithmetical proportion to the quantity of the same ingredient in the neutral compound. Potash, for example, combines with carbonic acid in a certain proportion, forming a neu-

* New System of Chemical Philosophy, p. 214.

tral salt which may be crystallized. If this salt be decomposed by muriatic acid, the carbonic acid disengaged assumes the aërial form, and from the volume it occupies, its quantity is determined. If this neutral compound be exposed to a red heat, part of its carbonic acid is expelled, but the quantity which it yields in this partial decomposition is exactly the half that it contained ; so that, when the new compound is decomposed by muriatic acid, it gives half the quantity of the carbonic acid which was afforded by the neutral salt, decomposed in a similar manner. The case, he found, to be the same with the compound of soda and carbonic acid. And in other compound salts, in a neutral state, and with an excess of acid, as in the sulphate and super-sulphate of potash, he found the neutral compound to contain just half the quantity of acid contained in the other. Dr Thomson had shewn, that the case is the same in the compounds of oxalic acid with potash and with strontites. Dr Wollaston having found, that this law with regard to relative proportions is observed in a number of such compounds, supposed it to be a general one, and was led to adopt, as including it, the more comprehensive principle stated by Mr Dalton, " That in all cases the simple elements of bodies are disposed to unite atom to atom singly ; or if either is in excess, it exceeds by a ratio to be expressed by some simple multiple of the number of its atoms *."

At a subsequent period Gay-Lussac brought into view another class of facts conformable to the same law. It had been known that in some cases aërial bodies combine in simple proportions estimated by volume. Thus the two airs, which are the elements of water, oxygen gas and hydrogen gas, combine in the proportion of 100 parts by

* Philosophical Transactions, 1808.

measure of oxygen gas with 200 measures of hydrogen gas. This led him to suppose that other gases might combine in similar simple proportions; and he accordingly found, both that this is the case, and that when two gases combine in different proportions, the larger proportion of the one has a simple arithmetical ratio by volume to the smaller proportion. Thus 100 measures of muriatic acid gas, he found, combine with exactly 100 measures of ammoniacal gas: fluoboric acid gas he found combined with ammonia in two proportions; one that of equal volumes of the two gases, the other that of 2 measures of the ammoniacal gas with one measure of the acid. Carbonic acid gas he farther found combined in the proportion of 100 parts with 200 of ammoniacal gas, forming a compound with excess of base; a neutral compound likewise exists, which, although it cannot be formed by direct combination of the gases, appears from analysis to consist of equal volumes of the two gases. These three acid gases, therefore, in combining with ammonia, unite with it in equal volumes to form a neutral compound; and two of them, in forming a different compound, unite with the ammonia in the proportion of one measure to two.

In proof that gases combine in very simple proportions estimated by volume, a number of other examples are given. 100 parts of ammonia are composed, according to M.A. Berthollet, of 200 measures of nitrogen, and 300 measures of hydrogen gas. Sulphuric acid is, according to the experiments of Gay-Lussac himself, composed of 100 measures of sulphurous acid gas and 50 of oxygen gas; and carbonic acid is composed of 100 measures of carbonic oxide gas and 50 of oxygen gas. The nitrous compounds give results when their proportions are reduced to volumes, whence a similar inference may be drawn, supposing slight errors in the experiment: admitting the corrections for these, the proportions (which however must be regarded as doubtful with regard to some of them) will be in ni-

trous oxide, 100 of nitrogen with 50 of oxygen, in nitric oxide 100 with 100, and in nitric acid 100 with 200. Oxy-muriatic gas consists of 300 of muriatic acid gas and 103 of oxygen gas, a deviation from the proportion of 300 to 100 extremely inconsiderable.

From all these facts, Gay-Lussac drew the conclusion, that elastic fluids in acting on each other combine in ratios the most simple, those which appear to exist in the preceding examples being of 1 to 1, 1 to 2, or 1 to 3 in volume. And it is farther to be remarked, he adds, (what distinguishes this from the doctrine of definite proportions, as maintained by Dalton and Wollaston,) that when the proportions are considered in weight, there is no simple ratio between the elements of the first combination; it is only when there is a second combination between the same elements, that the new proportion of that which has been added is a multiple of the first. The gases, on the contrary, in those proportions in which they can combine, always form compounds, the elements of which are in volume, multiples the one of the other *. The table which he has given exhibiting these results, with a table on the same subject by Mr Dalton, will be found at the end of the chapter.

Berzelius has generalized this result theoretically, by supposing that the same law would be observed in the combinations of all bodies, if they were reduced to the aerial form. All of them may either actually be reduced to this form by a temperature sufficiently elevated, or at least they may be conceived of as composed of particles between which repulsion would be established, so that they would exist in it, if no other chemical change connected with the operation of temperature prevented the result. And in this case, the same law he supposes would regulate their combinations as that observed in the combinations of those

* *Mémoires d'Arcueil*, tom. ii, p. 287

gases on which we can operate. The doctrine under this form constitutes what has been called the theory of volumes. It is evidently merely a modification of the other. In support of it Berzelius has brought forward a very extensive series of experimental results*.

Such are the facts which fall under the general proposition with regard to the limits which chemical attraction observes in the relative proportions in which bodies combine together. It remains to consider the theory of them.

* In a work published by Mr Higgins, a number of years ago, (*A Comparative View of the Phlogistic and Antiphlogistic Theories*, 1789,) some cases of chemical compounds are stated, in which the combinations are held to consist of one particle of the one body with one particle, two particles, three, four or five of another. In sulphurous acid a single particle of sulphur is supposed to be united with a single particle of oxygen, and in sulphuric acid with two particles of oxygen, (page 36.) Water is held to be composed of one particle of oxygen with one particle of hydrogen, and to be incapable of uniting to a third particle of either, (page 37.) In sulphuretted hydrogen the particles of sulphur are supposed to be to those of hydrogen as nine to five, (page 81.) And in the nitrous compounds he supposed one particle of nitrogen to be combined with two particles of oxygen, forming nitric oxide, one with three constituting red nitrous acid, one with four constituting the pale yellow acid, and with five forming colourless nitric acid, (page 133-5.) But in these statements there is no trace of any induction that this might be a general law of chemical combination: the opinion was not extended beyond these few cases, nor was it brought forward with any prominent distinction: it accordingly attracted no attention; and Mr Higgins himself never prosecuted it, nor announced it farther until he advanced his pretensions subsequent to the publication of Mr Dalton's system. He certainly therefore has little or no claim to the doctrine.

Annals of Philosophy, vol. 2. 3. 4. and 5.

They have been represented under very different points of view, involving some uncertainty even with regard to the extent to which they are established.

That in many cases of chemical combination there are certain fixed or uniform proportions, in which the bodies combine, and that in other cases there is little or no limitation with regard to proportion, were propositions admitted in a great measure as ultimate facts. Berthollet seems first to have endeavoured to explain them, and to bring them under one general law*.

From the consideration of that class of facts, which have been already illustrated, by which the influence of quantity of matter on the exertion of attraction is established, he had inferred the general principle, that any body acts on another in the ratio of its affinity and quantity. There is therefore no proportion at which attraction ceases to operate; its tendency is to act on all the particles of matter, and to combine bodies in all proportions; and hence, since limits in many cases are placed to its operation, and bodies are capable of being combined only in certain proportions, these limits must arise, and these proportions be established from the operation of external forces alone. Cohesion and elasticity, in particular, place limits to its exertion. The application of this principle may be best illustrated in reference to the preceding general cases of chemical combination.

Where combination is unlimited, the operation of the principle is of course apparent. This generally happens in the mutual action of bodies in the liquid form, when the result of their combination is a substance which exists in the same form. In these the attraction simply operates; there is no elasticity to counteract it, and the cohesion of liquids is so inconsiderable that it in general can have little

* Researches on Chemical Affinity. Essay on Chemical Statics.

effect. In some cases, however, where a very weak attraction operates, the degree of cohesion and the difference of specific gravity seem sufficient to counteract it, and to place certain limits to the combination, as in the example of sulphuric ether and water, the former not being dissolved completely in less than ten parts of the latter.

Where combination is unlimited to a certain extent, but then ceases, it is easy to trace the limitation which occurs, to the operation of external forces,—cohesion and elasticity. In the solution of a salt in water, for example, the mutual attraction is at first sufficiently powerful to overcome the cohesion of the solid, and hence the solution of the salt takes place; but as this proceeds, the attraction becoming weaker, conformably to the law (already illustrated,) that its force is in the inverse ratio to saturation, it is at length unable to overcome the cohesion, and an equilibrium is established between the two forces, at which any farther combination must cease. If heat be applied, however, its effect is to diminish the cohesion of the solid: the solution is therefore resumed, and an additional portion of the salt is combined with the water: this again ceases until the temperature is farther raised; and if this can be done, so as to overcome entirely the cohesion of the solid, without converting the water into vapour, the combination may be established in every proportion. In other cases, the influence of elasticity in thus placing limits to combination is equally obvious: An æriform body is at first condensed and absorbed by a liquid, from the mutual affinity being sufficiently strong to overcome the elasticity of the air, but the affinity becoming weaker as the combination proceeds, is at length incapable of producing this effect: if cold, or pressure, however, be applied, this, by counteracting the elasticity, and so far diminishing it, gives rise to an additional absorption; and the only limit to the effect of cold in this

respect is its communicating cohesion to the liquid itself. Other external forces sometimes place limits to combination, particularly great differences of fusibility and specific gravity. Two metals not differing greatly from each other in these properties, may often be combined by fusion in every proportion. If the difference in fusibility is inconsiderable, they may not combine, or the more fusible may unite only with a small portion of the other. And the influence of specific gravity is shewn in the fact, that in a mass composed of two metals which have been fused together, and allowed to become solid without agitation, the under portion frequently contains a larger proportion of the heavier metal than the upper does.

So far the operation of external forces is obvious in placing limits to the exertion of chemical attraction. But the cases most difficult of explanation are those where combination is established only in one, or in a few definite proportions. These Berthollet endeavoured to explain in the following manner.

The effect of combination is condensation arising from the approximation of the particles by their mutual attraction. This probably always takes place, though sometimes disguised by aggregation or change of form. It is farther found, in those cases where the effect can be observed with greatest precision, that the degrees of condensation from the combination of two bodies are different in different proportions, and that there is always one proportion in which it is greatest. If it is sufficiently great, it may, by the force of cohesion to which it gives rise, oppose the farther progress of the mutual action; it may also withdraw the product from the sphere of action; and may thus, from both causes, insulate the combination at a particular proportion.

In the case of substances in the fluid form, which by combination form a product which passes into the solid state, the operation is sufficiently conformable to this view.

The combination is limited to that particular proportion in which this occurs; and if the transition to the solid state is counteracted by sufficient dilution in a solvent, there is no evidence of any specific proportion being observed, but the two bodies act on each other in all proportions. If an acid and an alkali be largely diluted with water, so that the compound which they form in any proportion is retained in solution, they unite in every relative quantity in which they can be presented to each other; the acidity diminishing as the proportion of alkali is increased, and the alkaline power being enfeebled as the proportion of acid is augmented, while there is a medium proportion at which they are neutralized. But in all these stages there are equal indications of chemical combination, and a compound of fixed proportions is only obtained where the force of cohesion operates to cause its separation. Accordingly, if the quantity of water is not sufficient to retain it dissolved, or if the excess of water is dissipated so as to reduce it below this point, then a specific compound is obtained by precipitation or crystallization, and in some cases different compounds can even be established according to the extent of the evaporation. Generally the compound of least solubility is that which exists at the point of neutralization, the condensation probably being greatest at that point; and hence it is this compound which is obtained in the solid state: but sometimes it forms with an excess of one of the ingredients, particularly where this ingredient has a much greater tendency to solidity than the other; and sometimes both the neutral compound, and that with an excess, may be formed, according to the circumstances by which these forces are allowed to operate.

In the combination of substances in the aërial form, the same cause must operate, and frequently to a greater extent.

When a strong attraction is not exerted between the

particles of two aëriform bodies, their elasticity acts as an opposing force; they do not enter into intimate combination, but remain diffused, or very slightly united. But when more powerful attractions are exerted, and when these are favoured by the necessary circumstances, more intimate combinations are established, and these always in determinate proportions. In all combinations there is a certain proportion in which the condensation is greatest; and in the combination of aërial substances, the condensation is usually so considerable that it must oppose a greater force to the exertion of attraction beyond this, and hence will fix the compound at one uniform proportion. The combination, however, is not limited always to one proportion. Where the condensation is much greater at one proportion than at another, it probably will be so, as is exemplified in the formation of water from its gaseous elements; but where the condensation is less, and the degrees of it are more equal at certain relative quantities of the ingredients, combinations may be established at these different proportions, by the influence of the relative quantities of the substance, by elasticity, or cohesion, or by the operation of other external circumstances.

In the combination of an aëriform body with a liquid or solid, the condensation is greater in proportion as the attraction between them is strong: it proceeds to that extent at which the affinity, weakened in the progress of the combination, becomes not sufficiently powerful to overcome the elasticity. At this a fixed proportion is established; or, by arrangements of circumstances influencing either the elasticity of the air, or the cohesion of the solid, combinations at other proportions may take place. Such probably are the modes of combination of oxygen gas with metals. In other cases, the solid or liquid condenses indefinite successive portions of elastic fluid, to the point at which the elasticity or the cohesion cannot be farther

overcome by the affinity. This is exemplified in the absorption of gases by water, and sometimes by certain solids.

Lastly, in those cases where the solid or liquid, in combining with an air, passes into the aëriform state, limits are placed to the combination by the cohesion on the one hand, and the elasticity on the other, the affinity becoming weaker in the approach to saturation, and being at length unable to produce the farther change; and sometimes, especially where heat is applied, the combination becomes subject to the laws which regulate the action of elastic fluids; the condensation, which is the consequence, insulating it at a certain proportion.

While Berthollet thus assigned causes for the limits with regard to proportions in chemical combination, his views led him to consider these limits as not always strictly or necessarily observed, and to regard combination in many cases as indefinite, where it had been held to be definite. Acids and alkalis, for example, he supposed to be capable of combining with each other in all proportions; and the uniform compounds of them which are obtained in the solid or crystallized state, he supposed to owe this uniformity to the influence of the force of cohesion, by which their insulated existence is established. Metals he supposed, in like manner, to combine with oxygen in numerous or indefinite proportions; and hence he regarded metallic oxidation as indeterminate, or nearly so, from the minimum to the maximum, where it is not rendered uniform by the operation of other powers.

These opinions were not, however, altogether received by chemists. Proust had maintained the idea that chemical combination is in general fixed and invariable with regard to proportions, and in particular that metals are susceptible only of definite degrees of oxidation. The same idea is necessarily implied in Mr Dalton's system; for in this it is supposed, that either atom combines with

atom individually, or one atom with two, three, four, &c., and of course intermediate combinations, such as that of two with three, or two with five, are excluded. And, in the more limited inductions by Wollaston and Gay-Lussac, it is held that attraction is exerted either exclusively, or at least more forcibly, in certain relative proportions of the particles of bodies, than it is in others.

Berthollet's views are undoubtedly just to a certain extent. Attraction is in many cases unlimited with regard to proportions, as is exemplified in the mutual action of a number of liquids. In whatever relative quantities the two bodies exerting attraction are presented to each other, they unite with equal facility; the union is in every case accompanied with a change of density, and though they are of different specific gravity, they remain uniformly combined: in these therefore the principle of his theory is established. In others attraction is obviously limited by the operation of external forces, by the influence, in particular, of cohesion and elasticity, as is exemplified in the solution of a solid by a liquid, and the absorption of an aëriform body by a fluid in limited quantity. That the influence of these forces occurring at particular stages of a combination may arrest it at these, and thus give rise to specific proportions, cannot but be regarded as extremely probable; and this operation, in many cases of definite combinations, is apparent in the fact, that the proportion at which the combination is established is that at which the combination is greatest, or at which the greatest degree of cohesion is acquired.

It must also be admitted, however, that the explanations with regard to this last class of combinations are in some measure vague and obscure. It is also true that combination is more frequently established in fixed proportions than Berthollet had supposed. And, lastly, the law which is established with regard to combinations in definite proportions, that in these a certain simple ratio

exists, cannot be explained according to his doctrine, while it is sufficiently conformable to the other. It is a result which evidently cannot arise from the operation of external forces alone, and which proves that attraction, instead of being unlimited, is exerted with greater energy between the particles of bodies in certain definite proportions than in others.

Still there are some facts not altogether conformable to the strict sense of the law in the form under which it has hitherto been expressed. There are cases where determinate proportions are usually established ; and even where these have simple ratios to each other, yet by peculiar arrangements of circumstances, combinations of the same elements in other proportions may be established. Berthollet has, in the progress of the discussion, brought forward some examples of this kind. In repeating the experiments of Wollaston on the decomposition of the carbonates of potash and soda, he obtained the same results,—that the carbonate exposed to a red heat yields such a portion of carbonic acid, that just half the quantity which it contained remains combined with the base ; and he farther found, that there is a similar tendency in the combinations of this acid with lime and barytes. But he also found, that intermediate compounds may be formed and even obtained crystallized ; and farther, that the acid is not retained in combination with an uniform force, but is retained more strongly as its quantity diminishes ; and that there exists a compound with still less acid, than in the subcarbonate obtained by decomposing the carbonate by a red heat. In extending the experiments to other acids, he found that sulphuric acid forms with potash or with soda, acidulous salts, in which the excess of acid is very variable ; whence it appears that this tendency to unite in determinate proportions is very different in different substances *. There

* Mémoires d'Arcueil, tom. ii, p. 471, 482.

are other facts, from which it may be inferred that combinations are not invariably limited even where there is a tendency in the elements to definite proportions. In the mineral kingdom, for example, the ingredients in the same species admit of a considerable diversity in proportions. In the vegetable and animal proximate principles, this is often the case to an equal extent. And it is mere hypothesis, without much probability, to assume that in all these cases a few definite proportions only are established, which are disguised by intermixture or other accidental causes.

The highest approximation to the just expression of the fact on this subject seems to be,—that where weak attractions operate, and where the external forces of cohesion and elasticity do not interfere, combination is unlimited with regard to proportions,—that where these forces are present, they frequently place limits to attraction,—but that besides these, chemical action is in many cases exerted with more energy, where the bodies exerting it are in simple ratios with regard to each other, or in proportions which are multiples of these, so that combinations are established more easily, and are more permanent in these proportions than in others, this law being chiefly observed where powerful attractions prevail. There is thus a series nearly from unlimited combinations to those more strictly defined; while in all, the influence of quantity appears to operate to a certain extent.

I shall afterwards have to state some views of chemical theory, the prosecution of which leads to the conclusion, that the definite proportions, in which bodies are capable of entering into combination, are more numerous than have hitherto been supposed, or than can be easily obtained insulated. And if this be just, it will obviate still more completely the preceding difficulties, and reconcile the series of facts, which appear in opposition to each other,—those proving the limitation of chemical union to a few definite proportions in the elements of compounds, and those which

prove that combinations are much diversified, and proportions less strictly defined.

I have now to illustrate another important relation connected with this subject. Richter appears to have suggested the first idea of it in a law, which he announced from experiment, with regard to the compounds of acids with alkaline or earthy bases. “If two such compounds in the neutral state are mixed together, and produce mutual decomposition, the new compounds formed will, with scarcely any exception, be in the neutral state.” The respective quantities of the two acids existing in the two compounds being thus neutralized by the quantity of either of the one base or of the other, and in like manner the quantity of each base being neutralized by the quantity of either of the acids which the compounds contain, it is evident that a certain relation exists in the quantities of these substances producing neutral combinations, which can be discovered by the experiment. And by multiplying experiments on different compounds, the equivalent quantities of the different acids and different bases producing these neutral combinations may be determined. Richter accordingly gave an extensive series of tables from experiment, representing these, and exhibiting the composition of a number of saline compounds. Fischer remarked that these tables might be comprised in a single one with two columns, one containing the acids, the other the bases with numbers attached to each representing the quantities in which they produce mutual neutralization; 1000 parts of sulphuric acid, for example, neutralizing 1605 of potash, 859 of soda, 793 of lime, 672 of ammonia, 615 of magnesia, &c.: 712 of muriatic acid, 1408 of nitric acid, &c. neutralizing the same quantities, so that the whole could be reduced to any standard by the common rule of proportion *. And Berthollet remarked, that to assign the pro-

* Fischer's Table will be found at the end of the Chapter,

portions in these combination, it was only necessary to determine, first the proportions of one acid with the different bases, and then the proportions of a single combination of each of the other acids with any base, taking that which is most convenient, and an easy calculation gives the proportions of all the others *.

The principle, however, as displayed in these investigations, was under a limited application of it, and its importance was not sufficiently perceived, until it was generalized and placed in a more striking light, as implied in an hypothesis connected with a system of chemical combination which Mr Dalton proposed.

In this system combination is supposed to take place between the atoms or particles of bodies individually, one atom of one body combining with one of another, with two atoms, with three or with four. If this be admitted, and if it is known what the kind of combination is, we have a mode of determining, what, seems at first view to be beyond the reach of investigation,—the weights of the atoms of bodies. When only one combination of two bodies can be obtained, it must be presumed, according to Mr Dalton, to be a binary one, that is, to consist of one atom of the one body with one of the other. In this case it is obvious that the weights of these atoms must be as the weights in which the bodies combine, for the quantity of the one body contains, by the assumption, the same number of atoms that the quantity of the other does. The elements of water, for example, oxygen and hydrogen, can be combined together only in one proportion; the combination is therefore held to be a binary one, that is, one atom of oxygen combines with one of hydrogen. The proportion in which they combine is that of 80.3 oxygen and 12.7 of hydrogen by weight; that is, 7.5 to 1 nearly. The former quantity, therefore, containing, according to the hypothesis, the same

* Chemical Statics, vol. 1, p. 38. 400.

number of atoms as the latter, the weight of an atom of oxygen must be 7.5, that of an atom of hydrogen being 1.

When bodies combine in two definite proportions, if the proportion in the one is in a simple arithmetical ratio to that in the other, then it is evident that the same conclusion follows from either, conformable to Mr Dalton's rules; that is, the combination with the lowest proportion being held to be a binary one, or composed of one atom with one, the next must be held to be ternary, or composed of one atom with two, and from either the relative weights of the atoms may be inferred. Thus carbon combines with oxygen in the proportion of 43 to 57 by weight, forming carbonic oxide; and again in the proportion of 27.4 to 72.6, forming carbonic acid, the only two compounds of these elements known to exist. The proportion in the first is that of 5.6 to 7.5, that in the second is the proportion of 5.6 to 15 nearly. The first is held to be a binary compound, or composed of one atom of each element; the second is regarded as a ternary compound, or composed of one atom of carbon with two atoms of oxygen. From either, therefore, it follows, that the weight of an atom of oxygen being 7.5, that of an atom of carbon is 5.6.

The same results, too, are established by the different combinations into which a body enters. In the preceding example the weight of an atom of carbon is inferred from its combination with oxygen. It may equally be inferred from its combination with hydrogen. These elements unite in two definite proportions,—first in the proportion of 35 of carbon to 15 of hydrogen, forming olefiant gas, and secondly in the proportion of 74 of carbon to 26 of hydrogen, forming carburetted hydrogen gas. The former of these is the proportion of 5.6 to 1, the latter of 5.6 to 2. The first is held therefore to be binary, or to consist of one atom of hydrogen with one atom of carbon; the second is ternary, or consists of one atom of carbon

with two atoms of hydrogen; from either it follows that the weight of an atom of carbon is to that of an atom of hydrogen as 5.6 to 1. But the weight of an atom of carbon has been found to be to that of an atom of oxygen as 5.6 to 7.5, and the weight of an atom of oxygen has been found to be to that of an atom of hydrogen as 7.5 to 1; and hence all these results correspond: or, stating the weight of an atom of hydrogen, the element which enters in smallest quantity, as 1, the weight of an atom of carbon is 5.6, and that of an atom of oxygen 7.5.

In a similar manner, the weights of the atoms of other bodies may be determined, and this either from combinations with these elements, or with others, the proportions of which can be accurately determined. Mr Dalton traced an extensive system of this kind, applying it to the constitution of a number of chemical compounds; and Berzelius, who had entered on the investigation from attending to the law of Richter, Dr Wollaston, and others, have extended and corrected these researches *.

Now, independent of the particular hypothesis connected with this system, as to one atom of one body combining with one atom of another, with two atoms, three, or four, the facts unfold a relation of great importance, which appears to be established to a very considerable extent. It is, that each body enters into combination in one uniform quantity, or simple multiple of that quantity, in relation to certain constant quantities in which other bodies in like manner combine. Thus, in the preceding examples, it has appeared that hydrogen enters into combination in

* Dalton's New System of Chemical Philosophy. See also an excellent exposition of the doctrine by Mr Ewart in the third volume new series of the Manchester Memoirs; Dr Wollaston's paper, Philosophical Transactions, 1814, and several dissertations by Berzelius, and by Dr Thomson, Annals of Philosophy, vol. 2. 3. 4, and 5.

a quantity as 1, or its multiples, 2, 3, &c.; oxygen in a quantity, as 7.5, or its multiples, 15, &c.; and carbon in a quantity as 5.6, or its multiples, 11.2, &c. The same important result may be illustrated by some other examples.

Sulphur combines with hydrogen in the proportion of 93.8 to 6.2, that is, in the proportion of 15 to 1. Sulphur combines with oxygen in the proportion in one combination of 50 of sulphur and 50 of oxygen, constituting sulphurous acid; and in another of 50 of sulphur and 75 of oxygen, constituting sulphuric acid. Taking the number sulphur at 15, these proportions of oxygen are 15 and 22.5, which are the simple multiples of its primary number 7.5.

Copper combines with oxygen in the proportion of 100 to 12.5. Stating the oxygen at 7.5, this gives the proportion of metal at 60. There is another combination into which they enter, in the proportion of 100 of copper with 25 of oxygen. This gives the proportion of 15 of oxygen to 60 of the metal. Again, copper combines with sulphur in the proportion of 100 to 25, that is, 60 to 15. In all these, therefore, the relative quantity of copper is 60, that of oxygen being, as in the preceding cases, 7.5, or its multiple 15, and that of sulphur being 15.

Lastly, zinc combines with oxygen in the proportion of 100 with 24.4, which, stating the quantity of oxygen at 7.5, gives the proportion of zinc at 30 nearly. Again, in blende, the native compound of zinc and sulphur, the proportions are 100 of zinc to 48.9 of sulphur, which, stating the sulphur at 15, as in the preceding examples, gives also nearly the proportion of 30.

Thus, in all these cases, the quantities in which the bodies combine are in uniform relations to each other. In all of them hydrogen enters as 1, or its multiples, 2, &c.; oxygen as 7.5, or its multiples, 15, 22.5, &c.; carbon as 5.6, or its multiples, 11.2, &c.; sulphur as 15, or its multiples,

30, &c.; copper as 60; zinc as 30; and the same relation may be traced in many other combinations.

This relation is one evidently of the greatest importance, independent of any hypothesis which may be applied to explain it. At the same time it is desirable to assign a cause for it, if this can be done. Whence then, recurring to the theory of it, should this relation in the weights in which bodies enter into definite proportions exist? This Mr Dalton's hypothesis professes to explain.

His explanation is, that bodies combine atom with atom singly, or else one atom of one with two, with three, or with four atoms of another. The lowest of the quantities, therefore, in which a body enters into combination, denotes the weight of its atom, and the multiples of this denote two, three or four atoms; hence the constancy in which it combines in these quantities. The weight of an atom of hydrogen is relatively 1: in conformity to the principle, therefore, hydrogen must enter into combinations in a quantity as 1, or its multiples, 2, 3, 4. The weight of an atom of oxygen is 7.5; it must therefore enter into combinations in the quantity of 7.5, or its multiples, 15, 22.5, 30. And the same constancy must exist in the quantities in which other bodies combine.

There is, strictly speaking, no proof of the truth of this doctrine. Attraction may be exerted from atom to atom individually, or from one to two atoms, three or four; and this may constitute chemical combination. But it is equally possible that attraction may be exerted from a certain number of particles of one body to a certain number of particles of another, which number or a single multiple of it always enters into its combinations; and all that the fact of arithmetical ratios in successive combinations proves, is, that whatever number may enter into the first combination, twice that number enter into the second, three times the number into the third, and so on with regard to others. Either of these views accords, therefore, with the facts, and

for any practical inference they are the same, since it is the same thing whether one atom having a weight expressed by a certain number, or a number of atoms having this weight, uniformly enters into the combinations the body forms.

No cause, it may be said, is assigned on the last supposition, for the uniform relation in the quantities in which bodies combine; for there is no apparent cause why a certain number of particles should always be associated in the combinations into which a body enters. In the opposite system this is accounted for. The lowest quantity denotes the weight of the atom of the body, and the multiples of course denote two, three or four atoms. This is an advantage, therefore, belonging to Mr Dalton's view. But it is an advantage gained merely from a hypothetical assumption; and the subject is one in which little confidence can be placed in any speculations with regard to it. We have no means of judging of the relative weights or magnitudes of the atoms of bodies, or what number of them a given volume, or a given weight of a body contain: we have no means of determining, therefore, from the actual proportions in which bodies unite, what number of atoms of the one combine with those of the other, nor can we, on any certain grounds, draw any conclusion as to their modes of union. It may be the most simple hypothesis, that one atom combines with one, with two, three or four atoms; but it does not follow that this is actually the case; nor is there any evidence of its truth. On the contrary, it is equally possible that from the figures, magnitudes and attractive powers of the particles, such an equilibrium may be established, that a certain number of them may enter into union with those of another, and that twice or thrice that number may, from a similar influence, enter more easily into combination than any other intermediate proportion. The uniformity, therefore, in the relative quantities in which bodies combine, and the law of arithmetical ra-

tios existing in their combinations, may be as easily reconciled with the one system as with the other, and no superior probability can be attached to either. "When we recollect," says Mr Robison, in allusion to a different chemical speculation, "that the united efforts of all the mathematicians of Europe have not yet given a demonstrable and accurate account of the motion of three particles attracting each other, we can expect little success when we seek to determine the motion of millions of particles attracting at once."

The atomic hypothesis, when applied to the phenomena of chemical combination, will be farther found liable to difficulties of considerable importance.

In the more general doctrine, for example, that attraction is exerted from a certain number of particles of one body to a certain number of particles of another, so as to establish combinations with uniform proportions, it may be admitted, that from the influence of circumstances, the force exerted may be so far modified, that these proportions may be counteracted, and other combinations formed. But in the atomic system, one atom of one body must combine with one, two, three, or four of another, and any intermediate combinations cannot exist; in other words, the system maintains not only that combinations in definite proportions, and with simple arithmetical ratios in the different quantities of one of the ingredients exist, but that there can be no others; while, on the opposite doctrine, although it may be inferred, in conformity to the actual fact, that such combinations are usually established, still the possibility of the occurrence of others is not precluded. Now, there are many cases of chemical combination in which such deviations exist. I have already referred to some examples established by Berthollet with regard to those saline compounds, in which even the law of arithmetical proportions is observed, (p. 136.) There are numerous combinations in the mineral kingdom, in

which greater diversities of composition from the same elements are to be found. On the atomic system all such combinations must be denied, and the substances apparently exhibiting them must be held to be *mixtures* or compounds of other definite compounds in the proper proportions,—an assumption which is altogether hypothetical, and in many cases extremely improbable *.

Of the same nature are those numerous facts connected with partial decomposition, which have already been in part referred to, (page 77,) cases in which the greater part of an ingredient is abstracted from a substance with which it is combined, while a minute portion of it is retained in combination with a strength of attraction which the decomposing force cannot overcome. In submitting, for example, the compound of potash or soda with carbonic acid to the agency of lime, the greater part of the carbonic acid is abstracted; but a portion remains in combination with the potash or soda, which the lime cannot abstract. The

* One of the most striking examples of this is to be found in the substance named Minium, or red oxide of lead. Though possessed of properties perfectly uniform and characteristic, and though apparently of definite composition, it is held to be not a direct compound of the elements it affords, lead and oxygen, but a mixture or compound of the yellow and the brown oxide of lead. The yellow oxide is regarded as a compound of one atom of lead and one of oxygen; the brown oxide, from the proportion of oxygen it contains, compared with the other, must be held to be a compound of one atom of lead and two of oxygen. The red oxide of lead is of intermediate composition; and to avoid the absurdity of admitting $1\frac{1}{2}$ atom of oxygen, it is held to be not a compound of lead and oxygen, but of the yellow and the brown oxides. A similar assumption must be made with regard to some other metallic oxides. But it is obvious that this is without the slightest foundation, and is indeed a mere verbal distinction framed to obviate the difficulty.

compound operated on, the subcarbonate as it is called, is that which according to the atomic hypothesis consists of one atom of potash and one of carbonic acid; of course any remaining compound must consist of an atom of potash with less than an atom of carbonic acid, which is an absurdity. And if, to obviate this, a different view of the composition were given,—if the subcarbonate were supposed to consist of one atom of potash with two atoms of carbonic acid, so as to admit, in the progress of the decomposition, of its reduction to a compound composed of one atom of each, it is no such definite compound as this that does remain, but one with a much smaller quantity of carbonic acid; and a portion remains at length so minute, that regarding it as in combination with the potash, no view that can be given will bring it under the hypothesis. It is therefore necessary to maintain, that a portion merely of the subcarbonate remains undecomposed along with the solution of the potash. But this is assumed on no just ground. Since the lime abstracts the carbonic acid from one part of the subcarbonate of potash, it must equally abstract it from the other; and there is no cause whence one part of the compound should be decomposed, and the other not, when the whole is equally submitted to action.

A similar illustration may be derived from many cases of decomposition, in which a volatile substance is expelled by heat, but in which a minute portion of it remains with the fixed substance, inferior to the smallest relative quantity in which, according to the hypothesis, it can be supposed to combine with the other. Examples of this are to be found in the expulsion of carbonic acid from bases with which it is combined, or in the volatilization of water from certain saline compounds. The expulsion of hydrogen from charcoal in its common state of preparation affords one still more striking. It continues to be expelled according to the degree of heat applied; numerous successive portions are thus abstracted, which at the different

stages of temperature would have remained in combination ; and at the utmost intensity of heat a minute portion is still retained, which has been estimated not to exceed one part in 100 of charcoal. Now, considering the relative weight of an atom of hydrogen and that of an atom of carbon, the base of charcoal, and considering also the known definite compounds in which these elements exist, such a number of atoms of carbon must be held to be in union with an atom of hydrogen in these combinations as cannot be brought under the laws of the atomic hypothesis, and this too without any connection, by the intermediate multiples, with the known compounds. It must be held, therefore, that the hydrogen is not chemically combined with the carbon. Yet the proof of combination is as conclusive as that of any other combination of an aëriform with a solid body ; and the attraction producing it is even powerful, as is evident from the intensity of heat required to overcome it, and from its being even from the highest heat only partially overcome.

There are many examples, more particularly in the compounds of the mineral kingdom, and in those formed in the vegetable and animal systems, in which an ingredient is present in very minute quantity, but still is uniformly so, proving that it is essential to the composition. In such cases, if bodies are supposed to combine atom with atom individually, or one atom with two, three, or four, so large a number of atoms of one of the elements must be held to be combined with one atom of the other, as to exceed all probability ; sometimes, for example, the relation necessary to be inferred being that of one atom to 100, 200, or even a greater number *.

* Graphite or native carburet of iron affords an example. It is sometimes found with so small a proportion of iron as 3 in 100 parts. And from the relative combining weights of iron and carbon, it must be inferred from this that one atom of iron is combined with 250 atoms of carbon.

Lastly, a number of combinations have been discovered, in which from the proportions and the equivalent weights, it follows, that one atom of the one body is not combined with one or with two atoms of the other, but with the intermediate proportion of one and a half, an absurdity which evidently cannot be maintained. In some of these cases, the difficulty can be obviated by supposing that a lower proportion exists, (though the actual compound is unknown,) and that the series is that of one, two, three. But there are others, to which, from the relative equivalent weights, even this assumption cannot be applied.

So many cases, indeed, of this kind, and of those involving the other difficulties now illustrated, have occurred, that to obviate them, the defenders of the atomic hypothesis have admitted that combinations may exist of two atoms with three, with four, &c. But this admission is to relinquish the leading principle of the system, and to admit the opposite doctrine, that attraction may be exerted not from atom to atom individually, or from one to two, three, &c. but from a certain number of atoms of one body to a certain number of atoms of another; for if such combinations as those of two with three, or two with four, are established, to the exclusion of the more simple combinations of one with one, one with two, &c., then certainly there is nothing to prevent the conclusion, that they may exist in the relation of four with five, six with eight, or any other possible proportion whatever. It is also to relinquish the sole advantage which the atomic hypothesis claims,—that of assigning a cause for the uniformity of these relations; for no reason can be assigned why two atoms of a body should combine with three of another, more than why seven should combine with ten or any other number.

Some of these difficulties may perhaps be obviated in the progress of the science. There is, in particular, one important modification of the general doctrine, which I shall afterwards endeavour to shew falls to be established on

sufficient evidence,—that the definite proportions with simple arithmetical ratios, in which attraction is exerted between bodies, are much more numerous than those which give rise merely to the few insulated binary compounds which bodies in general form, and which have hitherto been observed. By the admission of this some of the most important of these difficulties may perhaps be removed. But still the atomic doctrine will remain an hypothesis, incapable of being established by any direct evidence, and involving all the disadvantages of a hypothetical system.

A body enters into chemical combination in a certain relative quantity to others, or in a simple multiple of that quantity. This is all that is established: it is a relation of the very first importance; and the expression of it ought to be distinct from all hypothesis, and from all theoretical terms. The term *combining quantity* may be employed as perhaps the most accurate; as it denotes simply the relative quantity, specific with regard to a body, in which it enters into combination with others; and the multiples of it may be expressed by saying the second, third, or fourth combining quantity. Or, as this quantity is equivalent to certain quantities in others, the term equivalent, or equivalent quantity, which has also been introduced, may be received; and the multiples of it may be expressed by saying two, three, or more equivalents. The hypothetical terms of atom in the system of Dalton, and volume in that of Berzelius, are synonymous with this. The term proportion cannot be admitted, as it has been established in chemical language in a different signification.

The labours of chemists have of late years been much devoted to the prosecution of this important subject, and the relations in the combining quantities of a great number of bodies have been determined. The results have been presented under different modifications. It is obvious, that to represent these quantities by numbers, a standard must be assumed to which they may be referred. Mr Dalton,

from the consideration that hydrogen is the element which enters, so far as is known, in smallest quantity into combinations, selected it as the standard, stating the weight of its atom (in other words its combining quantity) as unity : And considering water as composed of one atom of hydrogen with one of oxygen, the number representing oxygen is of course, from the relative quantities in which they combine, 7.5. Sir H. Davy followed Dalton in adopting hydrogen as the standard ; but from the circumstance that two volumes of hydrogen gas combine with one volume of oxygen gas to form water, he considered the compound as composed of two proportions of the one to one of the other : this therefore doubled the number representing oxygen, and, of course, the numbers representing the greater number of substances with which it combines,—a modification which, in this case, or in other cases of gases combining in simple proportions estimated by volume, might be considered as having some advantage, as in some measure expressing a fact, but which, as extended to other combinations, rests entirely on the arbitrary assumption, that equal volumes of gases contain the same number of atoms. Dr Wollaston, from the consideration that oxygen is the element which enters most extensively into combination, and which therefore is capable of affording, in the most direct manner, the quantities to be assigned to the greatest number of bodies, selected it as the standard, stating it at 10. Berzelius also assumed it as the standard, stating it at 100.

The reason which induced Mr Dalton to select hydrogen, that it is the element which enters into combinations in the smallest quantity, has some weight, as this undoubtedly affords the most simple and natural basis of the scale. But this is more than counterbalanced by the peculiar advantages attending the other : oxygen, as has been remarked, is the element which enters into the greatest number of combinations : hence the numbers of all the bodies with which it unites may be directly inferred from the pro-

portions in those combinations, while hydrogen unites with very few bodies, and the numbers in reference to it can only be found, therefore, in indirect modes. An important objection, too, exists to hydrogen, independent of this, that taking it as the unit, assigns fractional numbers to almost all other bodies. These reasons seem sufficient to give the preference to oxygen. In selecting it, the number assigned by Dr Wollaston is, on the whole, the most convenient one. To take 1, as some chemists, Dr Thomson in particular, have done, is more simple; but by taking 10, there is the advantage, that for those bodies whose combining quantities are below oxygen, such as hydrogen and carbon, integral numbers are given, though in some of them with fractional parts, while in the other they are all fractional. The number of 100 taken by Berzelius is unnecessarily high, and renders nearly all the other numbers inconveniently so. It is very desirable that chemists should refer to one standard without any variation: that of Dr Wollaston is on the whole preferable to any other; and it is farther recommended by the convenience derived from his sliding scale of chemical equivalents, which is adapted to it.

There will be found, at the end of this chapter, the table of Dalton, which, although it admits of corrections, from more accurate results of recent analyses, is interesting in some measure as the one originally given; and also the table on which Dr Wollaston's scale of chemical equivalents is founded, this being in fact a scale of combining quantities. The former is in relation to hydrogen as 1, the other to oxygen as 10, taken as a standard. The numbers on the one scale are easily reduced to those in the other. To convert those of Wollaston into those of Dalton, multiply the number in the former by 7, and divide by 10. To convert those of Dalton into those of Wollaston, multiply the number in the former by 10, and divide by 7. From the most accurate estimate, however, of the proportions of

the elements of water, on which the relation in quantity between oxygen and hydrogen is inferred, 7.5 is the number which, according to Dalton's scale, ought to be assigned to oxygen, rather than that of 7, which is the number he assigns; and accordingly the numbers referred to his standard are by some chemists given conformable to this. To these tables I have also added one given by Berzelius*. It refers to oxygen as a standard, stating its number at 100; and differs in its construction, therefore, from that of Wollaston only in the decimal point.

Sometimes the numbers assigned on different authorities do not strictly correspond, independent of the apparent difference, from the standard referred to. This arises from two causes. One is the variation in the results of analysis, so that from different proportions, different numbers must be assigned. Thus, in the composition of water, one proportion which has been given is that of 87.4 of oxygen and 12.6 of hydrogen; another is 88.3 of oxygen and 11.3 of hydrogen. According to the former, the number belonging to oxygen is to hydrogen as 7 to 1, according to the other it is 7.5. Such differences will gradually be removed as the experimental results are determined with more precision. Another cause of diversity arises from the point of view under which the combination of two bodies is considered. The one may be held to be in the relation to the other of one atom to one, or of one atom to two atoms, or conversely in that of two atoms to one, that is, expressing the fact, independent of any hypothesis, the one may be considered in combination with the other in its lowest proportion, or in a multiple of this, the lowest being perhaps unknown, though there may be some grounds to believe it exists, as in like manner the other body may be in one or other of these relations. Now in these cases the numbers assigned will be different. But this arises merely from the

* *Annals of Philosophy*, vol. iii, p. 362.

uncertainty with regard to the series of combinations ; and the difference must be that only of taking half or double of a certain number in the one case from what is taken in the other.

From the results of the investigations on this subject, it appears that certain relations exist between the combining quantities of bodies and their chemical constitution. Those of the metals, for example, are usually large, that is, the substances of this class enter in large proportions, compared with other bodies, into the compounds they form. No compound, for example, of a metal with oxygen is known, in which the oxygen exceeds the metal ; in all of them the reverse is the case generally to a considerable amount. The combining quantities of inflammables are less. Those of compounds too are greater than those of their elements, as is conspicuous in acids or in alkalis compared with their elements, or in compound salts compared with the acid or base of which they are formed. At the same time, these relations are not perfectly strict, and there are many cases in which the combining quantities of bodies, extremely different in their chemical constitution, are nearly the same.

The laws which have now been illustrated, are of the greatest importance in chemical science, and have given it in some measure a new aspect. They introduce calculation to the aid of experiment, both in leading to investigation, and in correcting the errors or supplying the deficiencies of analysis. Thus, from our knowledge of the arithmetical ratio existing between the different proportions in which a body combines with another, it may with reason be presumed, if in any of these combinations analysis has assigned a proportion approaching to, but not altogether conformable to this, that the deviation arises from inaccuracy, and the proportion inferred by calculation may be assigned. The same law may sometimes indicate a knowledge of compounds,—as, for example, where a series of compounds of two bodies exist, in which one of them is

present in the ratio of one, two, four, it may with probability be inferred, that a compound also exists in the intermediate ratio of three, and a more strict examination may discover it. The relation of the combining quantities of bodies admits of a still more extensive application to the discovery of their composition and combinations ; for from our knowledge of the relation in which a body exists in certain combinations, we discover that in which it must exist in others, even through an extensive series of substances ; and may assign even its precise proportion. We are thus enabled, by equivalent numbers, to apply results which admit of facility and precision to others, which are attended with difficulty and error. It is only necessary to guard against the too extensive application of the principle, independent of actual investigation, and to keep the results of calculation always subordinate to those of experiment.

There are some subordinate rules connected more or less strictly with these relations, which are of importance in these applications.

The law pointed out by Gay-Lussac already illustrated, that gases combine in simple proportions by volume, is obviously one of this kind, and it affords a very important principle in investigating the constitution of gaseous compounds.

The law announced by Richter, which has also been noticed, that when two neutral salts produce mutual decomposition, the two new salts which are formed are equally neutral, depends on the relation in the combining quantities of the respective acids and bases producing neutralization, and affords the most important aid to experiment in determining the composition of neutral salts. This application of it will fall to be considered more at length under this subject.

Richter announced another general fact, that when a metallic salt is decomposed by another metal, and the metal

of the former is precipitated, the oxygen and the acid are equally transferred to the new metal, forming a new salt, in which, whatever may be the quantity of metal, the oxygen and acid retain the same proportion. Gay-Lussac hence expressed the general law,—that the quantity of acid in metallic salts is directly proportional to the oxygen in the base of the salt; and as the fixed alkalis and the earths are, strictly speaking, metallic oxides, this applies to the whole of these bases, and the application of it facilitates the investigation of almost all saline compounds. To this Berzelius has added another,—that the quantity of oxygen in the base and that in the acid have a certain simple relation, being either equal, or the oxygen in the acid being double, three, or four times the quantity in the base: or, expressing it more generally, When two bodies enter into combination, each containing oxygen, the quantity of oxygen in the one is always a multiple by a whole number of that in the other. The application of these laws will be considered under the general statement of the composition of saline compounds, the subject with which they are more peculiarly connected.

In the practical application of the law of arithmetical proportions in chemical combinations, and of the relation of the combining quantities of bodies, great advantage is derived from an instrument contrived by Dr Wollaston, what he has named the Scale of Chemical Equivalents. It consists of a scale of numbers on the principle of Gunter's scale, moveable, so that any number can be placed opposite the names of a series of substances in an adjoining column, arranged in the order of their relative combining weights, in such a manner that the number denoting the combining weight of a body being placed opposite to its name, 10, for example, opposite to oxygen, the numbers expressing the combining quantities of others will be found opposite to their names. It thus shews, too, the equivalent combining quantities of all bodies with re-

gard to each other, whatever proportions be employed; for, supposing a number denoting a certain quantity to be placed, by means of the slider, opposite to the name of a body, 25, for example, opposite to oxygen, then the quantities of the others equivalent to this will be found opposite to their names. This instrument is delineated, Plate VI. Its mode of construction will be explained under the statement of the Table of combining quantities, on which it is founded, at the end of the chapter.

By this instrument a number of important results are obtained by mere inspection. If it is wished, for example, to know what quantity of one body combines with another, it is shewn by the respective numbers which will be found opposite their names. If the composition of any compound, with regard to the proportions of its elements, is to be determined, the slider is to be so placed that the number 100 is opposite to its name, and the respective quantities of the ingredients will be found opposite to their names; or if it is wished to know the proportions in any other quantity than that of 100, by placing the number denoting this quantity opposite to the name of the compound, they will be in like manner found. If a compound is to be decomposed by the agency of a substance exerting an attraction to one of its ingredients, on placing a number denoting a certain quantity, suppose 100 of the compound, opposite to its name, the quantity required of the decomposing substance will be indicated in a similar manner, and the quantity of the new compound which it forms will be found by the number opposite to its name. All these results may equally be obtained from the scale in the plate, by reducing the numbers to any required standard by the common rule of proportion. But the convenience of the instrument itself is, that it exhibits them by the movement of the slider, without any calculation; and hence the facilities it affords in practical chemistry.

II. Of the limits to attraction with regard to the number of substances which may be brought into simultaneous combination.

Chemical attraction is not equally exerted among a number of substances placed within the sphere of action, so as to cause them to pass uniformly into combination. With regard to this certain limits are observed, which diversify the states of union.

If three substances are placed within the sphere of chemical action, it generally happens that two of them combine, to the exclusion of the third; or sometimes one is combined with each of the others, being divided between them in proportions determined by their affinities and quantities, so as to form two distinct compounds. In some cases, however, instead of either of these varieties of combination, the three substances have their affinities mutually balanced, in such a manner that they enter into simultaneous combination. Even four, five, or perhaps more substances may thus be combined. Such combinations are named Ternary, Quaternary, &c. according to the number of their constituent parts.

Of these combinations there are numerous examples among the metals. If three or four metals be fused together, they often unite, and form one uniform compound. We have also frequent examples of ternary combinations among saline compounds, one acid being saturated by the joint action of two bases. Nature, too, presents us with a number of such compounds. Mineral substances usually consist of three, four or five ingredients. Nearly all the substances belonging to the vegetable kingdom are composed of at least three principles; and the composition of the animal products is still more complicated, four or five principles being combined in their formation.

These combinations appear to take place principally among bodies having mutual attractions, which, under given circumstances, are nearly of the same force, and where

the binary compounds they would form do not differ much from each other in cohesion, or the other qualities which influence combination. Did the attraction of one ingredient to any of the others much exceed their mutual affinities, it would probably give rise to an insulated binary compound; or did the force of cohesion or elasticity operate with much energy on any of the substances in their mutual binary combination, this might modify the reciprocal action. But where neither of these circumstances is present, the affinities may be balanced, and give rise to one combination. Hence, probably, their formation more peculiarly in the vessels of vegetables and animals, where, from the constant motion and agitation to which they are subjected, the compression under which they are placed, and the smallness of the mass in which the affinities operate, the circumstances of cohesion, elasticity and quantity are prevented from operating, and an equilibrium of affinities is more easily established.

There is another point of view under which these combinations may be considered. When three elements are present, it may be supposed that they are not in direct combination, but that one of them is combined with a certain portion of each of the others, and that the two compounds thus formed are combined together, forming what may be denominated a Sur-compound; and where four elements exist, indeed, of simultaneous combination, they may in like manner be combined two and two, forming compounds in this state of sur-composition. It is scarcely possible to determine between these two opinions, for there is no mode of discovering the state of combination. It is not improbable that in some cases the one mode of combination exists, in others the other. This may be inferred from the properties of the compound, which seem sometimes to be the modified properties of the binary compounds, in others have no relation to these. Still even this evidence is not altogether conclusive.

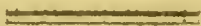
When a ternary compound is resolved by decomposition into binary compounds of its elements, the combinations are in the definite proportions which the elements usually observe, and no excess of either remains. This was shewn by Gay-Lussac*. The triple salt known by the name of Rochelle Salt, the tartrate of potash and soda, consists of potash, soda, and tartaric acid mutually neutralized; and these are in such proportions as to constitute, when they are brought into a different state of combination, the two binary compounds, tartrate of potash, and tartrate of soda, without any excess. The case is probably the same with all triple neutral salts, and seems necessarily to be so as a consequence of the relation in the combining quantities of bodies; for in a ternary combination containing two bases, each of these will require as much of the acid for its neutralization as it will in the binary combination. It may even be extended to all ternary compounds, and it may therefore probably be expressed as a general law, that “in ternary combinations, the elements are united in such proportions, that when the combination is subverted, they unite two and two, (one of the ingredients in certain portions combining with each of the others,) and form binary compounds of the same definite composition, as they form when they are separately combined.” Nor does this at all prove either of the above opinions, the result being equally conformable to the principle, that the three elements are in direct combination in the compound, or that it consists of the two binary compounds.

When compounds containing four ingredients are decomposed by the existing combinations being altered from the elements entering into other states of union in different proportions, the new compounds are in general equal-

* *Annales de Chimie*, tom. 77; *Nicolson's Journal*, vol. 31.

ly definite, and are formed without any excess or deficiency of any of the elements. The salt named nitrate of ammonia is composed of oxygen and nitrogen in the state of nitric acid, and of hydrogen and nitrogen in the state of ammonia; when decomposed by heat, it is resolved entirely into the two new definite compounds of oxygen and nitrogen, and oxygen and hydrogen, forming water and nitrous oxide; and the whole is the result of the uniform relation of quantity in which bodies combine.

Sometimes, however, both in ternary and quaternary compounds, from the diversity of proportions in which the elements are capable of combining, there may remain an excess of one of the ingredients,—an example of which is to be found in the analysis of the vegetable products, in which charcoal very generally remains in excess.



SECT. V.—*Of the Forces with which Chemical Attraction is exerted.*

ALL the phenomena of chemistry concur in proving, that different bodies exert different forces of affinity; and could these forces be accurately determined, the science might rest on the basis of calculation. The subject of the present section is therefore interesting, though it is at the same time somewhat complicated and obscure.

It is first necessary to explain the doctrines of Single and Double Elective Attraction, the phenomena of which have usually been referred to the relative forces of affinity exerted among bodies. In consequence of the attractions which one body has to others, numerous combinations may be formed; but these attractions can be so far overcome, by those exerted by other bodies, that these combinations can be subverted, and the compounds formed decomposed. And this has been supposed to arise from

the attraction exerted by one body being more powerful than that exerted by another to a third.

If A have to B a force of affinity, which, under given circumstances, is equal to 6, they will unite, and form the compound AB. But if C, a third body, have an attraction to A, which, under the same circumstances, is equal to 8; it will, when presented to the compound AB, decompose it, and form a new compound AC, and B will be separated in an uncombined state. Decomposition, it is evident, would equally take place, if C, instead of exerting a superior attraction to A, exerted it to B; these two will combine, and A be separated.

This forms what the chemists have named Single Elective Attraction. Every substance has attractions towards others, and is, therefore, capable of combining with them. But it does not exert the tendency to combination with the same force to all; to some it is greater than to others, and to each it is different in its degree. If, therefore, a body be combined with one to which it has a weak affinity, the compound which is formed will be decomposed, by the addition of any other to which it has a stronger attraction; the two combining, between which the attraction is strongest, and excluding the other. Hence arises an extensive series of decompositions, and hence is derived the power which the chemist has of recovering the substances he has combined together, and of obtaining also the simple elements of which the products of nature are formed.

In these cases of single elective attraction, there is often a partition of action, whence the decompositions are not complete. When the compound AB is decomposed, by C exerting an attraction to A, it often happens that though A is in a great measure abstracted, a portion of it remains combined with B; and it is principally where the agency of C is strongly favoured by the circumstances influencing chemical action, that a complete decomposition of AB

will be obtained. Frequently, too, the ingredient excluded, attracts a portion of the decomposing substance, and is from this cause not obtained pure.

When differences in the relative forces of attraction were observed, it was an obvious idea to construct tables in which they might be represented. This was first done by Geoffroy, a French chemist, in 1718, and the labours of many chemists have been directed towards correcting and extending these tables. Their construction is simple. The substance, whose attractions are to be enumerated, is placed at the head of a column, and the substances to which it has an attraction are placed beneath it, in the order of their relative forces, that to which it has the strongest attraction being immediately under it, the others following in this order, and the one to which it has the weakest attraction of course closing the column. Thus the attractions of lime and of muriatic acid are represented in the following tables.

LIME.	MURIATIC ACID.
<hr/>	<hr/>
Oxalic acid.	Barytes.
Sulphuric acid.	Potash.
Tartaric acid.	Soda.
Phosphoric acid.	Lime.
Nitric acid.	Ammonia.
Muriatic acid.	Magnesia.

Bergman undertook the task of extending and correcting the tables of elective attraction ; and since his time some additions have been made to them. Though their utility may be questioned, in their full extent, yet as conveying some information on the order of decomposition, under given circumstances, in many cases of chemical action, I have inserted them at the end of this chapter.

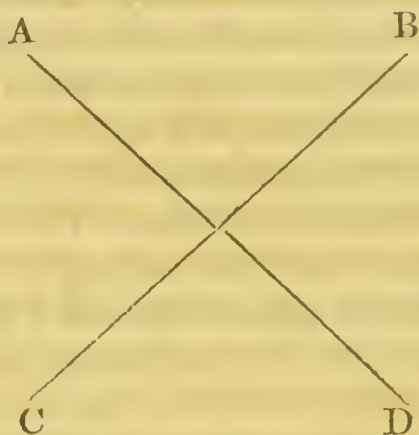
There remains to be explained another case of elective attraction, more complicated.

On mixing together two compounds, it often happens that the combination of each is subverted; they exchange their principles, and by the new combinations into which these enter, other compounds are formed. If two bodies, A and B, have existed in combination in one compound, and other two bodies, C and D, in the other, A leaves B and combines with D, C at the same time combines with B, and the new compounds AD, CB are thus produced. Now, this decomposition of either compound could not have been effected by the single attraction of either of the elements of the other, but only by their joint attraction; while these are at the same time modified by the attraction the two bodies exert to each other. The whole result may thus be illustrated. If in the compound AB, the force of attraction exerted is equal to 20, and if the attraction of A to D is equal to 16, it is obvious that no decomposition will ensue; A cannot leave B to enter into union with D. But suppose that D is united with C, with a force of attraction equal to 7, and suppose that C has an attraction to B equal to 12, then on mixing the two compounds AB, CD, the decomposition of each will take place; for the sum of their existing attractions tending to preserve their principles in union is inferior to the sum of those tending to separate them; the former, the affinity of A to B and the affinity of C to D, being $20 + 7 = 27$; the latter, the affinity of A to D and of C to B, being $16 + 12 = 28$. AB, CD, therefore, are decomposed, and two new compounds, AD, CB, are formed.

This is what is termed, in the language of chemistry, Double Elective Attraction; two elective attractions being exerted, and two new compounds formed. Of the two attractions which are exerted, the tendency of the one is to preserve the original compounds undecomposed, that of the other is to separate their principles. The former were

named by Kirwán, the Quiescent; the latter, the Divellent Attractions. It is evident, that a double decomposition can only be effected where the sum of the divellent is superior to that of the quiescent attractions.

To represent more clearly and concisely what passes in these complicated attractions, diagrams have been constructed. The idea seems first to have occurred to Dr Cullen. The one he proposed was, that of two cylinders crossing each other at the middle.



If on mixing the compounds denoted by AC, BD, the attractions of A to B, and of C to D, overcome the quiescent attractions, AC, BD; the resulting decomposition is represented, by supposing the extremities AB, CD, of the cylinders to be brought together; by which also the production of the two new compounds will be denoted by the conjunction of these letters.

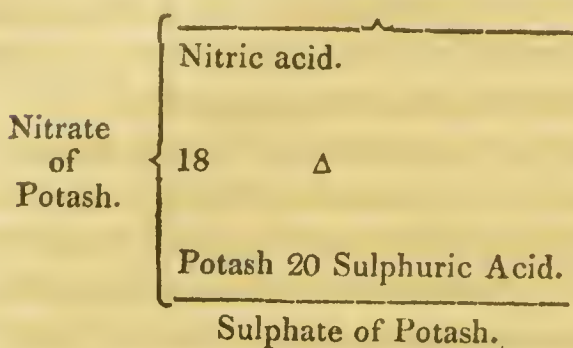
The diagram proposed by Bergman consists of two brackets connected by straight lines, forming a square, at the sides and corners of which, the names of the compounds and of their ingredients are placed, and is better calculated to represent the concomitant circumstances of the operation.

Muriate of Potash.

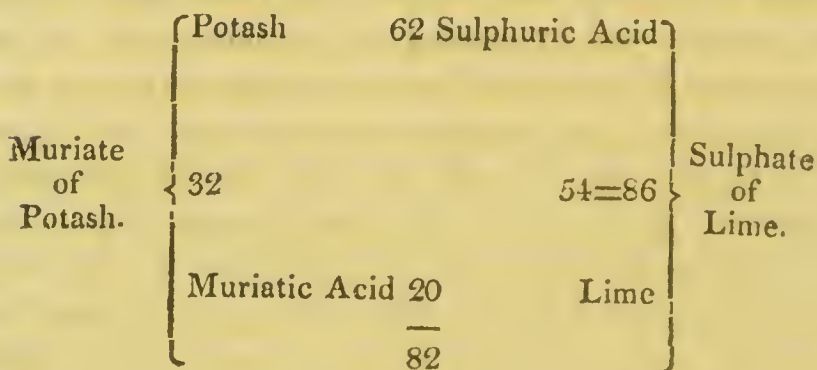
Sulphate of Potash.	Potash.	32	Muriatic acid	Muriate of Lime.
	62	Δ	20=82	
	Sulphuric acid	54 — 86	Lime	
	Sulphate of Lime.			

Thus in the scheme which Bergman gives, if the two compounds, named Sulphate of Potash, and Muriate of Lime, the former consisting of sulphuric acid and potash, the latter of muriatic acid and lime, be mixed together, a double decomposition takes place, and two new compounds, Muriate of Potash, and Sulphate of Lime, are formed. This is represented by placing on the outer sides of the two brackets the names of the two compounds mixed, and at the corners of the brackets the names of their ingredients, so disposed that the one acid shall be diagonally opposite to the other. If the numbers expressing the relative force of attractions of the principles of these compounds be added, it will be obvious that a decomposition will ensue. The attraction between potash and sulphuric acid being 62, and that between lime and muriatic acid 20, the sum of the quiescent attractions is 82. But the attraction between potash and muriatic acid being 32, and that between sulphuric acid and lime 54, the sum of the divellent attractions is 86. These, therefore, will operate with effect; the muriatic acid and the potash will combine together, as will the sulphuric acid and the lime; and the names of the resulting compounds, muriate of potash and sulphate of lime, are placed without the straight lines, by which the brackets are connected.

To represent a single elective attraction, the same figure is used, with one bracket, as in this diagram.



Where the quiescent attractions are superior to the divellent, and no decomposition takes place, the scheme consists of two unconnected brackets, with the names of the compounds at each side, and of their ingredients at each corner; the numbers, denoting the forces of attraction, being interposed.



By some additions various circumstances connected with these decompositions are represented. Thus, it frequently happens, that one or both of the new compounds are insoluble, and consequently fall down. This is denoted by bending downwards in the middle, the line placed between the substance and the square, as in diagram 2, where the undermost line is bent down to shew that the Sulphate of Lime is precipitated. If one of the substances be volatilized or sublimed, the line is bent upwards in the middle, as

in diagram 3, where the upper line is drawn in this manner to shew that the Nitric Acid is volatilized. If they are neither precipitated nor volatilized, the brackets are connected by straight lines. The circumstances under which the decomposition takes place are also pointed out. Sometimes it is effected by the substances being dissolved by water, sometimes by the application of heat to them in the solid state. Bergman distinguished this, by inserting in the middle of the diagram a triangle, Δ , which was the old chemical sign for fire, to denote that the decomposition was effected in the dry way, or by the application of heat; and an inverted triangle, ∇ , the sign for water, to point out when it was done in a watery solution. The same method is still used, the symbols only having been changed, a perpendicular line $|$ being that for caloric or heat, and the compound figure, H , for water. To facilitate the construction of such diagrams, all the chemical agents have been distinguished by particular symbols.

The important general fact attending these decompositions has been shortly noticed at the end of the preceding section,—that the state of neutralization remains unchanged. If two compounds, in each of which the ingredients are combined to the point of neutralization, are mixed together, and a double decomposition ensues, the two new compounds which are formed are equally neutral, (at least unless one of them has a very strong tendency to form with an excess of acid or of base.) This shews such a relation between the proportions of the substances and their power of producing neutralization, that the quantity of one which neutralizes the base with which it is combined in the one compound, will, when transferred to the base of the other, neutralize the quantity of it which the ingredient detached from it had neutralized; while this, on the other hand, will be equally capable of neutralizing the quantity of base with which the other had been combined. It is a consequence of the relation in the combining quantities of bodies

already illustrated, and it leads, as is afterwards to be stated, to an accurate method of determining the composition of saline compounds.

Such are the doctrines of single and double elective attraction, as they were delivered by Bergman, and generally received by chemists. A different view was given by Berthollet of these changes, which remains to be explained.

In Bergman's theory, affinity is regarded as an invariable force producing combination; and decomposition is the consequence merely of the predominance of stronger over weaker attractions. The strength of attraction may therefore be inferred from the order of decomposition. In the theory of Berthollet, the changes are referred to the operation of those circumstances by which attraction is influenced. If the substances which act on each other be liquid, or be soluble in the fluid which is the medium of action, and if the compounds they form have no great cohesion or insolubility, no evident change appears when they are mixed, there is a mutual saturation, and the opposing substances, it is conceived, remain united, forming an individual combination, in which the forces are balanced. But if, on any of the parts of such a combination, the force of cohesion or insolubility, or the power of elasticity operate with energy, these external forces subvert the balance, give rise to separations, and hence are the real cause of the results which in the other theory are ascribed to the predominance of divellent over quiescent affinities.

The effect of chemical combination is condensation. If substances are placed within the sphere of mutual action, which in combining with others suffer considerable condensation, so that a strong force of cohesion is acquired, this may determine their combination to the exclusion of others, and insulate the compound which is thus formed. In a case of double decomposition, where four substances

are presented to each other, if two of them having a mutual attraction have a greater tendency to cohesion than the others, or form a compound of sparing solubility, and the other two a compound of a different nature; instead of the four forming one combination, in which the affinities are balanced, the equilibrium is subverted by the force of cohesion, and the two which form the insoluble compound will combine together, and be separated by precipitation or crystallization, the other two remaining in combination in the fluid which has been the medium of action. If even these four substances were previously in the reverse binary combinations, still on presenting them to each other, the affinities within the sphere of action must be reciprocally exerted, and the same extraneous forces will cause an exchange of principles; in other words, if A and B when united form an insoluble compound, and C and D one that is soluble; if A has been previously combined with C, and B with D, the result on mixing these two compounds will not be reciprocal saturation and a simultaneous combination, but the force of cohesion operating with more energy on the combination of A and B, it will separate, while the other two ingredients, C and D, will remain in union *.

* "In a solution," says Berthollet, "of sulphate of potash and muriate of soda, these two salts are not distinct, nor do they become so until some external cause produce their separation: sulphuric and muriatic acids, potash and soda are combined in the liquid." "If," he continues, "a solution of sulphate of potash be mixed with a solution of muriate of lime, the lime brought into contact with the sulphuric acid will be more powerfully influenced by the force of cohesion than the potash. It is therefore a force in addition to those which pre-existed, and determines the combination of the sulphuric acid with the lime, and the precipitation of the new compound." Cases of this kind he denominates Complex Affinity, to avoid the term Elective Attraction, which in some measure implies an hypothesis.

The same principle is applied to a single elective attraction, or where three substances are presented to each other. If the combination of two of them give rise to a substance of sparing solubility, or having a strong tendency to cohesion, this circumstance will determine their union, and the separation of the insoluble compound, instead of the balance of affinities of all the three substances which would otherwise have been the result.

Hence, as Berthollet remarks, “if all the decompositions ascribed to complex affinities be investigated, it will be found, that the prevailing affinity has been ascribed to those substances which have the property of precipitating, or of forming a salt which can be separated by crystallization. For this reason, it may be inferred *à priori*, from a knowledge of the solubility of salts, which may be formed in a liquid, that those substances which are least soluble will be found to be the same as those to which Bergman and other learned chemists have attributed the strongest affinity in their tables *.”

Other decompositions, particularly those where the application of heat is necessary, are occasioned by the operation of elasticity. Thus, if one of the ingredients of a compound have a tendency to assume the elastic form,—then on submitting the compound to the action of a substance capable of combining with its other ingredient or base, its decomposition is not to be ascribed with Bergman to the predominance of a powerful affinity over one more weak, but to the tendency of the elastic ingredient to escape from its combination, which aided by the intervention of another affinity, not only not stronger, but even weaker, may occasion the separation. In double decomposition this is not less effective, the elevated temperature determining the union of the substances most disposed to

* Researches into the Laws of Chemical Affinity, p. 106.

assume the elastic form, and their separation as a volatile compound. “ If, therefore, it be desired to know the result of the exposure of two salts to the action of heat, it is only necessary to consider which of the two bases, and which of the two acids, have the greater volatility, if there be a difference ; for the more volatile base and acid will escape, and enter into combination, and the fixed base and fixed acid will remain behind, and combine with one another *.”

Such is the view given by Berthollet of what are named Single and Double Elective Attractions, and there can be little doubt that much of it is just. A strong argument in support of it is the one which Berthollet adduces, that in the usual order of elective affinities, superior forces have been ascribed, among the acids, to those which form salts having the greatest tendency to cohesion, as the sulphuric, the phosphoric, tartaric, and oxalic ; and among the bases, to those which form the least soluble compounds, as lime, barytes and strontites ; and in the very exceptions in the order of the strength of affinities of these acids and bases, we find, that where weaker affinities have been ascribed to them, it has been in those cases where they form soluble salts. “ Lime, magnesia, strontites, and barytes, form insoluble salts with carbonic acid. All the soluble salts of these earths, mixed with alkaline carbonates, produce an exchange, from which result the formation and precipitation of an earthy carbonate. Barytes forms an insoluble salt with sulphuric acid ; therefore whenever a solution of a sulphate is mixed with that of a salt of barytes, there will be a precipitation of sulphate of barytes. As sulphate of lime is but little soluble, and consequently much disposed to precipitate, lime decomposes all the soluble sulphates to that term at which the precipitation is stopped by the solubility of the sulphate of lime. But sulphate of lime

* Researches, p. 3.

being much more soluble than sulphate of barytes, the salts of barytes, which are more soluble than the sulphate of lime, decompose it *." The same relations may be traced among the metallic salts. And even where the force of cohesion is not exerted on any of the parts of the combination with such effect as to give rise to precipitation, still, when favoured by the evaporation of the liquid which has been the medium of action, the superior affinity will always be found to have been ascribed to the constituents of that salt which is first separated by crystallization. Thus, in all these cases, decompositions arising from the separation of substances, in consequence of their insolubility in the liquid in which chemical action was exerted, have been ascribed to predominance of strength of affinity.

In like manner, those acids which have the greatest tendency to assume the elastic state, have been considered as exerting the weakest affinity, because they are more easily separated from the combinations in which they exist. And for the same reason, in decompositions produced by heat, the weakest affinity among the alkaline or earthy bases is in the tables of elective attraction ascribed to ammonia, which is the most volatile ; while among the acids the most powerful attractions are assigned to the sulphuric and phosphoric, which are the most fixed.

Relative quantity of matter, or the proportion of one substance to another, has also an influence in determining these combinations ; and hence the results are much dependent on the proportions of the substances mixed, especially where the external forces of cohesion and elasticity do not operate with much power, so as to render imperceptible the effect of quantity. Berthollet has accordingly shewn, from a number of examples, that in mixing compound salts where cohesion does not interfere with

* Chemical Researches, p. 167.

much force, a predominance of attraction may be ascribed to either of the acids or bases according to the proportions in which the substances are mixed together *. It is likewise shewn, that in cases of this kind, there is a succession of combinations determined by the proportions, degree of solubility, and mutual action of the salts, and different from each other, so that an error would be committed if we should suppose that the products of successive crystallizations in such mixtures will be the same as the first.

These facts are undoubtedly in favour of Berthollet's theory, and prove that the results of single and double decompositions are not owing, as had formerly been supposed, to the predominance of strong over weaker attractions. Yet the question is not without difficulty, both with regard to the principle of the theory, and to the operation of the circumstances by which the changes are supposed to be produced.

With regard to the principle, that in a case where three or more substances attracting each other are within the sphere of action, simultaneous combination must be established, and that binary compounds can be formed only from the operation of external forces, this is certainly no necessary conclusion, and it is not established by any evidence. Differences in the strength of affinity among bodies exist; and such differences, it may be inferred, will give

* When two parts of muriate of lime and one of nitrate of potash were mixed, muriate of potash was obtained by crystallization; but when equal weights of nitrate of potash and muriate of lime were mixed, the first product by crystallization was nitrate of potash. From the result of the first experiment, it would have been concluded, that in these salts the divellent were superior to the quiescent affinities; from the result of the second, the conclusion would have been precisely the reverse. *Chemical Researches*, p. 169.

rise to binary combinations, independent of the influence of such forces. In the case of single elective attraction, in which two acids are brought to act on one base, it is admitted that the forces of affinity of these acids to the base are different. May not this determine the manner and proportion in which they combine, or cause the acid which has the stronger affinity to combine exclusively with the base, independent of any external force, or at least principally with it, while the other acid combines with a smaller portion of base? If either compound have much tendency to cohesion, it will separate; but it does not follow that its cohesion is the cause of its formation. This may be determined by the superior force of affinities in its principles; it is only the separation of it that is produced by the cohesive power; and the compound thus separated may either be that in which the principles are united by the strongest, or that in which they are united by the weakest attraction. Or in the example of complex affinity, two acids and two bases being present, if no foreign force is exerted, they will form, according to the theory of Berthollet, one combination, both acids contributing to the saturation of both the bases. But suppose that one of the acids has a stronger attraction to one of the bases than the other acid has; and suppose also that the latter acid has a stronger attraction to the base to which the other acid has a weak affinity; will not the result of this be, that the acids will be divided between these bases in proportion to their affinities towards them? If no cohesion or elasticity is exerted, these binary compounds will not appear, for there is scarcely any property by which they can be detected. But it may be maintained that they must be formed; and it is their appearance only, not their production, that is determined by the exertion of elasticity or cohesion. Hence is explained the observation, which Berthollet regards as proving his opinion,—that in complex

affinity, the prevailing attraction has always been ascribed to those substances which form a compound that passes to the solid form ; for, in other cases, though the binary compounds might be formed, they would not be obtained insulated, and therefore the predominance of affinity would not be observed. At the same time it must also be acknowledged, that it does not follow, on this theory, that the insoluble compound should always be formed.

One cause may be assigned as preventing binary combinations,—the affinity which in the mixture of two compound salts the bases may reciprocally exert, and the affinity which the acids may exert to each other, which may counteract the affinity of the one base to the one acid, and of the other to the other, and, added to the quiescent affinities of the acids to the bases, prevent the divellent ones from operating, and establish one combination. But these affinities in general appear weak : admitting that they may be in some cases sufficiently powerful to prevent the binary combinations of the acids and bases, it is not probable that they will always be so ; and where they are not, binary combinations must be established from the different affinities of the acids to the bases.

Berthollet has stated, what he considers as a proof of his opinion, that “ when two compound salts are mixed, the mutual decomposition of which would produce combinations of very different proportions, neither a redundancy of acid or of base, which would necessarily result from such decomposition, can be observed. This has been very judiciously observed by Guyton. A change of base therefore does not take place*.” But it is taken for granted, that in these cases the proportions of the constituent principles of these salts are known with perfect accuracy, which is not the case, and the result observed by Guyton is a proof of this. Indeed the mutual saturation ought to re-

* Chemical Researches, p. 108.

main the same, whether one combination or two binary ones be formed, because the sum of the reciprocal forces of the acids and bases remains the same, at least unless one of the salts has a strong tendency to form either with an excess of acid or of base. If calculations from the proportions of the ingredients of the salts mixed shew that there ought to be an excess either of acid or of base, this only proves that the proportions have been inaccurately determined; and it accordingly now appears, that in these cases inaccurate proportions had been assigned.

The question can only be determined by the comparative probability of the respective assumptions *à priori*; for it is scarcely possible to prove either of them by experiment. Whether binary compounds are formed in a liquid or not, can be known only from their separation; and when this happens, it must, on either hypothesis, be ascribed to the force of cohesion or elasticity; so that we cannot say whether they had existed previous to the exertion of that force. And, on the other hand, if there is no separation, by what property or appearance shall we discover whether the principles exist in a mutual state of saturation forming one compound, or whether they form principally binary compounds, which remain in solution? In considering the comparative probability of the hypothesis, it appears to follow, that if four substances are brought together, a difference in the forces of their affinities may prevent an uniform combination, and by causing those which have the strongest affinity to combine, may give rise to the formation of binary compounds and to the phenomena of elective attraction. The influence of external forces with regard to these may at the same time be admitted: they will either concur with the differences of affinities in the formation of the compounds, or counteract their operation. The commencement of the combinations may arise from differences in the forces of affinity; while if, on any of the binary combinations thus formed, cohesion or

any other force producing its separation be exerted, this will favour the completion of the combination, by withdrawing the principles from the action of the others.

Still, although this reasoning appears to be just, it is not altogether satisfactory; for it does not account for the striking fact, that in *all* cases single and double decompositions take place, where elements are present which form insoluble compounds, and always in such a manner as to establish these compounds. There is no apparent relation between the insolubility and the force of affinity to account for such a result, and it seems to prove that the former is the effective force. The same observation evidently applies to the influence of elasticity, in the cases in which it operates.

On the other hand, there are considerable difficulties with regard to the mode of action, according to which these external forces can produce the results. On the assumption, that when three or four substances are presented to each other, they would form a simultaneous combination, were not some external force, such as that of cohesion, exerted, it is difficult to discover how this force can operate in giving rise to binary combinations. Its operation may be conceived to be, either on the *principles* of the combination causing those which have the greatest tendency to cohesion to combine together, or on the *compound* itself producing its separation, and thus withdrawing its elements from the action of the other bodies. It is not very clear, from the language of Berthollet, under which of these views he regards the influence of cohesion. But either of them is inadequate to the explanation of the phenomena of complex affinity, on the assumption that the relative forces of affinity have no share in giving rise to binary combinations.

Thus, considering the first of these assumptions,—that of four principles presented to each other in a common fluid, the two having the strongest tendency to cohesion will be

those which will be combined, we do not perceive, since all the substances are in a state of solution, how the cohesion alone can combine two of them. The immediate result of their attractions, it is supposed, is to form one combination. From the density resulting from that compound, such an addition might be made to the force of cohesion as to cause it to separate; but we perceive no reason why this should give rise to the binary combination; while, if that combination were determined by the superior force of affinity, it is easy to perceive that the separation of the compound might be produced in consequence of the accrued condensation. Nor in appealing to fact do we find that in such mixtures the principles which are combined are always those which, in their insulated state, have the greatest tendency to cohesion. They sometimes are so, but in many cases this cannot be observed.

This leads to the consideration of the other point of view, under which the influence of external forces on the results of complex affinity may be regarded,—that of four principles in solution, the two which will be combined (leaving of course the other two in binary combination) are those which form an insoluble compound; or that when the mutual action is effected by heat, the two which combine are those forming a volatile compound. This accords better with facts. But in adopting it we fall into the inconsistency of assigning a property of a compound as the cause of the formation of that compound. If the result, independent of foreign forces, is to form an individual combination, this cannot be disturbed by any force which would act, if that combination were subverted, and binary compounds formed. The insolubility or volatility of a compound is a property dependent on its constitution,—on the relation of its *integral particles* to the force of cohesion, or to the repulsive agency of heat; and it must have been formed before they can be called into existence. There must be some cause to produce these compounds before

any influence can arise from any property of which they are possessed.

Some facts, it has been already stated, (page 82,) have been brought forward, in proof that elective attractions exist producing exclusive combinations, and that the results must be ascribed to difference in strength of affinity, independent of the influence of external forces. They rest principally on the authority of Pfaff. He submitted tartrate of lime to the action of such a portion of sulphuric acid as was sufficient merely to neutralize the lime, and he found that the whole lime was transferred to it, and the tartaric acid obtained pure. In this case, therefore, there was no participation, but the exclusive combination of a base to an acid in opposition to another acid, and this without the influence of any external force to determine the result; for the force of cohesion or insolubility is not more powerful in the new compound, the sulphate of lime, than in the tartrate, but the reverse; and the tartaric acid remains in solution. The result therefore is strictly conformable to the doctrine of elective attraction. He found, that oxalate of lead was decomposed by a quantity of sulphuric acid capable of neutralizing exactly the quantity of oxide of lead which the oxalate contained; and this result is equally independent of, or is rather in opposition to, any influence that could arise from the force of cohesion, as oxalate of lead is even less soluble than sulphate of lead. On the other hand, magnesia triturated with, or even boiled in a solution of sulphate of potash to dryness, and heated strongly, did not abstract the smallest portion of sulphuric acid: with sulphate of soda, and with muriates of potash and soda, the results were the same*.

But though these experiments appear at first view conclusive, they have been very well explained by Berthollet himself†, who has pointed out circumstances connected with

* *Annales de Chimie*, tome 77, p. 259. † *Ibid.* p. 288.

them to which Pfaff did not attend. In the first case, the decomposition of tartrate of lime by sulphuric acid, although it is true, as Pfaff remarks, that tartrate of lime is less soluble in water than sulphate of lime, yet, as Berthollet remarks, the tartrate is rendered much more soluble by acids than the sulphate is: hence, therefore, in the experiment, the tartrate of lime is first rendered soluble by the portion of its acid which is liberated by its partial decomposition, while the sulphate of lime which is formed, not having its solubility augmented, its force of cohesion insulates it, and separates it from the liquid, and the decomposition is thus at length rendered complete. In like manner, to obviate the supposition of any effect from the force of cohesion in the production of sulphate of lead from oxalate of lead by sulphuric acid, Pfaff remarks, that the oxalate is even less soluble than the sulphate. It is so in water. But Berthollet finds that it is much more soluble in acids, and therefore, when an acid is evolved, as is the case in the experiment which Pfaff gives, the greater insolubility of the sulphate favours its progressive formation, and renders the decomposition of the oxalate complete. The circumstance of the magnesia not decomposing a soluble sulphate is evidently to be ascribed to its force of cohesion, and to the solubility of the alkaline base.

These facts, then, can scarcely be considered as forming any just exception to the theory of Berthollet. And even were it found, that where a considerable difference in the force of affinity exists, and where this is not opposed by the influence of external forces, combinations are established from it alone, this does not exclude the operation of these forces where they act with energy, or where differences of attraction less important exist. There is some difficulty, it may be admitted, in conceiving clearly of their mode of operation. And there is perhaps a deficiency in the theory, in not admitting the influence of the differences in strength of affinity among bodies; for since such differences

exist, they must, we should be disposed to believe, necessarily operate in the combinations which take place. Yet if even this be allowed, their operation seems to be of inferior importance, and can scarcely be clearly traced; while the striking facts, that in all those cases in which binary combinations are established among three or more bodies by the medium of solution, the affinities exerted are such as to form the least soluble compounds, and that in those effected by heat, they are such as to form the most volatile compounds, seem to prove that the external forces which modify attraction are those which principally determine the results.

Another subject which has occupied the attention of chemists, is that of determining the absolute forces of affinities among bodies. The usual measure of these forces is that deduced from decomposition; we infer from it, that one body, A, has a stronger attraction to another, B, than a third, C, has, because when BC are combined, A decomposes the compound, by attracting B. But admitting the justness of the inference, (which the preceding observations, however, prove to be incorrect,) we learn nothing more, than that the attraction of one body is stronger than that of a third. The desideratum is to know how much stronger it is; and were this done, it has been supposed that we might discover, by calculation, what we can at present ascertain only by experiment. Different methods have been followed in the attempts to solve this problem.

Guyton had observed, that different metals, when brought into contact with quicksilver, adhere to it with different degrees of force; and he found, that the order of the forces of adhesion corresponds with the known affinities of the metals to quicksilver. The experiment was made by bringing plates of the metals, of the same size and form, sus-

pended from the extremity of the beam of a sensible balance, into contact with mercury, and sliding them along its surface, the mercury being changed at each experiment. The force with which they adhered was discovered by the weight necessary to raise each plate.

Gold adhered to mercury with a force of 446 grains.	
Silver,	429
Tin,	418
Lead,	397
Bismuth,	372
Zinc,	204
Copper,	142
Antimony,	126
Iron,	115
Cobalt,	8

Guyton justly observes, that these differences cannot be owing to the different degrees of polish; for a plate of iron, unpolished, adhered more strongly, than one of the same metal finely polished: nor to the densities of the metals; for they are not proportional to these. But the order of adhesion is that of the apparent order of affinities; gold being the metal to which quicksilver seems to have the strongest attraction; while, with iron or cobalt, it can scarcely be combined. Hence these differences may be regarded as numerical expressions of the different forces of attraction. Experiments of this kind, however, were even the principle just, are too limited to be of much utility under this point of view; and when extended to other chemical agents, so many difficulties occur from mutual chemical action, and other causes, that the results admit of no strict conclusion. In the further experiments of Achard on the same subject *, we accordingly find a number of

* Encyclopédie Methodique, tom. 1, p. 468.

facts incompatible with the hypothesis. The principle also is doubtful, as the results denote rather the facility of combination than the force of attraction; and they might farther be modified by the combination at the surface of the metals, and perhaps by electric action.

Wenzel had supposed, that the quantity of a body dissolved in a given time affords a measure of the force of the affinity exerted. The method by which he proposed to apply this principle was to cover equal cylinders of different metals with a crust of varnish, leaving one extremity uncovered, and immersing them in a common solvent, such as nitric acid: according to his statement, the quantities dissolved in a given time correspond with the known affinities of the metals to the acid. But independent of objections, to which the experiment is liable, the principle is false. The facility or rapidity of combination depends not on the force of affinity, but on that modified by the cohesion, elasticity, and other qualities of bodies; and we have many examples, in which a combination takes place slowly, where the attraction from which it arises is strong, or where it is effected with facility, where the attraction is comparatively weak.

The resistance opposed by a combination to the separation of its constituent parts, has been proposed as the measure of the strength of their reciprocal affinity. But we have no means of appreciating the resistance with accuracy. The intervention of a superior affinity cannot be employed; for the strength of this would first require to be ascertained. And in employing heat there are many compounds which cannot be decomposed by heat; and in those which can, the decomposition is influenced as much by the comparative elasticity of the principles of the compound, as by the degree of attraction between them.

Mr Kirwan presented a view of this subject, different from any of the preceding, and probably more just. Among the chemical properties of bodies, there is frequent-

ly one which is predominant, and which gives to the substances possessing it a common and well-marked character. Of these characteristic properties some are opposed to each other ; one class of substances possessing one, another possessing the opposite. Thus the characteristic properties of the class of acids are the reverse of those of the class of alkalies. In the combination of two bodies belonging to these opposite classes, the adverse properties neutralize each other, and at a certain stage they disappear, or a compound is formed in which neither predominates. This is termed the point of neutralization or saturation. Now, this power of producing neutralization may be considered as arising from the force of affinity which the body exerts, and may therefore be regarded as a measure of that force. This occurred to Kirwan ; though in order to reconcile the principle with the established order of elective attractions, he adopted it only partially. From experiments on the composition of the neutral salts, he discovered that a relation subsisted between the quantities of their elements necessary to saturation, and their apparent forces of affinity ; and in prosecuting his experiments he was led to establish as principles,—First, That the quantity of real acid necessary to saturate a given weight of each base, is inversely as the affinity of the base to the acid ; and, secondly, That the quantity of each base requisite to saturate a given quantity of each acid, is directly as the affinity of the acid to the base. The quantities of the different substances necessary to produce saturation, he found, according to these principles, to correspond nearly with the apparent forces of attraction estimated from the usual order of decomposition. And he farther gave examples of decompositions strictly conformable to the forces of attraction thus inferred *.

* Philosophical Transactions, vol. lxxiii, p. 38.

In prosecuting the investigation, however, this correspondence was not always found to occur. On the contrary, decompositions were known to take place which ought not to happen, if the numbers expressing those forces of affinity were just. This indeed does not strictly prove the fallacy of the principle on which the method is founded, since such deviations may arise from errors in the estimation of the proportions of the ingredients of the compound salts, and there can now be no doubt of the existence of such errors, both as the experiments were liable to important sources of fallacy, and the results were vitiated by having been combined with assumptions which Kirwan afterwards found to be inaccurate. Resuming his labours, he accordingly gave, in the fourth and seventh volumes of the *Irish Transactions*, corrected and more extensive tables *, in which the numbers are entirely different. But though more accurate, they accord less strictly with the apparent forces of affinity, as inferred from the order of decomposition; and deviate indeed so much from this, that Mr Kirwan appeared to have relinquished the hope of attaining by this method the solution of the problem.

The views of Berthollet, however, throw more light on this subject; they lead to the conclusion, that were the numbers more remote than they are from the usual order of elective attractions, this is no proof that they may not express the real forces of affinity; since decompositions from which that order has been inferred, arise not merely from different strengths of affinity, but from these modified by various external forces. Hence attractions, which appear in experiment strong, may be weak; and others, which appear feeble, may be comparatively strong; nor, if the real order of the forces of affinity should be deduced from any principle, is there reason to expect that it should correspond with the results of decomposition.

* These will be found at the end of the Chapter.

Berthollet therefore disregarding this order, adopts the more general principle. As the reciprocal neutralization of substances combined is the effect of their affinity, it may be regarded as the measure of that affinity; and as unequal quantities of different substances are requisite to neutralize any common base on which they act, the forces of their affinity to that base, considering them as acting in equal quantities, must be different, and may be estimated from the quantities requisite to produce neutralization. Kirwan admitted the principle, that the affinities of the different acids to the same base is in the inverse ratio of the quantity of each of them which is necessary to neutralize an equal quantity of that base, or that the less of an acid requisite to produce the neutralization, the more energetic is its affinity, or the greater its force; but finding that were it also applied to the affinities of the bases to the acids, it would be inconsistent with the observed order of elective attractions, reversed it as applied to these bases, and thus subjected his hypothesis to a contradiction; that, on the one hand, it supposed a greater affinity to require a less quantity of a substance to produce saturation, and that, on the other, it required a greater quantity. Berthollet applies the same principle to both cases, and therefore the law now stated with regard to the affinities of the acids to the bases with which they combine, equally holds with regard to the affinities of these bases to the acids; or the base, which in the smallest quantity neutralizes an acid, is that which exerts to it the strongest attraction. It is to be extended to all other bodies, and the general principle therefore is, that the affinity of any substance to another is more powerful, as a given weight of it can neutralize a greater quantity of that other. Referring for illustration to its application to the different acids and bases, it follows, that of the acids, carbonic has the strongest attraction to alkaline bases, as the smallest quantity of it compared with other acids neutralizes a given weight of

them. Next to it is the muriatic, then the phosphoric, sulphuric and nitric. With regard to the bases, ammonia must exert the most powerful attraction, as a smaller quantity of it saturates given quantities of the acids; next to it are magnesia and lime, then soda and potash, and, lastly, strôntites and barytes.

These arrangements of the forces of affinities deviate widely from the received order. To connect the one with the other, it is necessary, Berthollet remarks, to seek in the habitudes of the substances which combine, and in the conditions in which they may be found, the explanation of the facts which lead to conclusions so opposite. It is to the force of cohesion and of elasticity more particularly, the effects of which have been confounded with those of affinity, that the deviations are to be ascribed. Barytes has been considered as exerting the most powerful attraction, merely because it produces decomposition by the insolubility it acquires in combination; and ammonia has been considered as having the weakest, because from its volatility it is most easily detached.

That no strict coincidence is to be looked for in the order of decompositions, and in the real scale of affinities on whatever principle the latter may be indicated, seems a proposition perfectly just. But some doubt, it appears to me, may be entertained with regard to the principle assumed in the preceding reasoning. The proposition is, that the less of one substance is required to neutralize the properties of another, the stronger is its attraction towards it. Since a smaller quantity of ammonia than of barytes is required to neutralize a given weight of sulphuric acid, the ammonia, it is inferred, exerts a stronger action on the acid than the barytes does, or exerts towards it a stronger affinity. But all affinity is reciprocal. The attraction which unites an acid and a base, so as to neutralize the properties of each, cannot be said to be a force exclusively exerted by the base to the acid, or by the acid to the

base. It is a mutual tendency in the particles of these two bodies to combine, and the quantity of the one necessary to neutralize the properties of the other cannot be regarded as an indication of the energy of action or strength of affinity exerted between them, unless the one substance were the active power that produced neutralization, and the other passive. But this is not the case; the attraction and neutralization are reciprocal; and we may as well take the quantity of acid necessary to neutralize a given weight of base, as a measure of the force of affinity, as the quantity of base necessary to neutralize a given weight of acid. The above statement would then be reversed; and it might be said, that since a smaller quantity of sulphuric acid is required to neutralize a given weight of barytes than to neutralize the same weight of ammonia, therefore the affinity is stronger between this acid and barytes than between it and ammonia. If this reasoning is just, it renders doubtful the preceding conclusions.

It must also be evident, that we can no longer look for those advantages from the solution of the problem of estimating the forces of affinity, which were formerly expected from it. While affinity was regarded as an uniform force, it was imagined, that were its intensities discovered, we might be able to predict the results of its exertion independent of experiment. But it is obvious, that were we even in possession of the scale of affinities, we could not foretell, in any given case, what would be their results, since they are modified by external circumstances, which totally alter their relative forces. We probably could not subject to calculation the complicated effects of cohesion, elasticity, quantity, and other modifying powers; and we should therefore be altogether unable to foresee the effective forces that would be exerted.

From the preceding observations it must be apparent, that the common tables of elective attractions do not represent the relative forces of affinity, but only a series of decompositions, which arise as much from the operation of circumstances which influence attraction, as from differences in the strength of the power itself. Nor do they even express the order of these decompositions with accuracy, since the influence of quantity, which undoubtedly modifies the results to a certain extent, has been neglected in the experiments on which they are founded. They are therefore of less utility than has been believed. As they may be condensed, however, in a short space, and may sometimes be consulted, I have given them a place. Those inserted are Bergman's, corrected by Dr Pearson. Their construction is simple. Each column represents the affinities of the substance, the name of which is placed at the head, to the substances the names of which are inserted beneath, in the supposed order of the strength of these affinities: those which are at the head of the column having stronger attractions to it than those beneath, and therefore decomposing the compounds of those beneath. Thus, from the first table it is understood that carbon exerts the strongest attraction to oxygen, and will therefore decompose all the compounds which oxygen forms with the others. Zinc is placed next; it, of course, will not decompose the compound of oxygen with carbon, but will decompose the rest. No better proof can be given of the uncertainty of these tables, than what happens to be afforded by this first example; for although in the table zinc is inferior to carbon in its attraction to oxygen, yet it decomposes partially the compound of carbon and oxygen; and carbon, on the other hand, can be made to decompose the compound of oxygen and zinc,—merely as the circumstances are changed under which these substances are made to act.

TABLE OF AFFINITIES.

I. OXYGEN.	Platina Mercury Silver Gold	VII. SULPHURETTED HYDROGEN.	IX. BARYTES.	XI. LIME.
Carbon			Acids	Acids
Zinc		Barytes	Sulphuric	Oxalic
Iron	III. NITROGEN.	Potash	Oxalic	Sulphuric
Hydrogen		Soda	Succinic	Tartaric
Manganese		Lime	Fluoric	Succinic
Cobalt	Oxygen	Ammonia	Phosphoric	Phosphoric
Nickel	Hydrogen	Magnesia	Saccho-lactic	Saccho-lactic
Lead		Zircon	Nitric	Nitric
Tin	IV. HYDROGEN.		Muriatic	Muriatic
Phosphorus		VIII.	Citric	Fluoric
Copper			Tartaric	Arsenic
Bismuth	Oxygen	AMMONIA, PO-	Arsenic	Citric
Antimony	Sulphur	TASH AND SO-	Benzoic	Benzoic
Quicksilver	Carbon	DA.	Acetic	Acetic
Arsenic	Phosphorus		Boracic	Boracic
Sulphur	Nitrogen	Acids	Sulphurous	Sulphurous
Gold		Sulphuric	Nitrous	Nitric
Silver	V. CARBON.	Nitric	Carbonic	Carbonic
Platina		Muriatic	Prussic	Prussic
Muriatic Acid	Oxygen	Fluoric	Sulphur	Sulphur
	Iron	Phosphoric		
	Hydrogen	Oxalic	X. STRONTITES.	XII. MAGNESIA.
		Tartaric		
	VI. SULPHUR.	Arsenic	Acids	Acids
		Succinic	Sulphuric	Oxalic
		Citric	Oxalic	Phosphoric
		Benzoic	Tartaric	Sulphuric
	Oxygen	Acetic	Fluoric	Fluoric
	Potash	Saccho-lactic	Nitric	Arsenic
	Soda	Boracic	Muriatic	Saccho-lactic
	Iron	Sulphurous	Succinic	Succinic
	Copper	Nitrous	Phosphoric	Nitric
	Tin	Carbonic	Acetic	Muriatic
	Lead	Prussic	Arsenic	Tartaric
	Silver	Water	Boracic	Citric
	Bismuth	Oil	Carbonic	Benzoic
	Antimony	Sulphur	Sulphur	Acetic
	Quicksilver			Boracic
	Arsenic			Sulphurous
	Molybdena			Carbonic
	Tellurium			

This is Vauquelin's table of the affinities of oxygen for metals, founded on the difficulty with which their oxides are decomposed by heat.

Prussic Sulphur	Alumina Metallic Oxides	XXIII. ARSENIC ACID.	XXX. ACETIC ACID.	Acetic Succinic Prussic Carbonic Ammonia
XIII. ALUMINA.	XVIII. SULPHUROUS ACID.	Lime Barytes Strontites Magnesia Potash Soda Ammonia Alumina Metallic Oxides	Barytes Potash Soda Ammonia Lime Magnesia Alumina Metallic Oxides	XXXIV. OXIDE OF PLATINA.
Acids Sulphuric Nitric Muriatic Fluoric Arsénic Oxalic Tartaric Phosphoric Acetic	Barytes Strontites Lime Potash Soda Magnesia Ammonia Alumina Metallic Oxides	XXIV. OXALIC ACID.	XXXI. PRUSSIC ACID.	Æther Acids Muriatic Nitric Sulphuric Arsénic Fluoric Tartaric Phosphoric Oxalic Citric Acetic Succinic
XIV. SILEX.	XIX. PHOSPHORIC ACID.	The same as in NO. 19.	Potash Soda Ammonia Lime Barytes Strontites Magnesia Alumina Metallic Oxides	XXXV. OXIDE OF QUICK-SILVER.
Fluoric Acid Potash	Lime Barytes Strontites Magnesia Potash Soda Ammonia Alumina Metallic Oxides	XXV. TARTARIC ACID.	XXXII. OXIDE OF GOLD.	Acids Muriatic Oxalic Succinic Phosphoric Arsénic Sulphuric Saccho-lactic Tartaric Citric Nitric Fluoric Acetic Boracic Prussic Carbonic
XV. ACIDS NITRIC AND NITROUS.	XX. CARBONIC ACID.	XXVI. CITRIC ACID.	Æther Acids Muriatic Nitric Sulphuric Arsénic Fluoric Tartaric Phosphoric Prussic	
Potash Soda Barytes Strontites Lime Magnesia Ammonia Alumina Metallic Oxides	Barytes Strontites Lime Fixed Alkalis Magnesia Ammonia Alumina Metallic Oxides	XXVII. BENZOIC ACID.	Fixed Alkalis Ammonia	
XVI. ACIDS MURIATIC AND OXYMURIATIC.	XXI. FLUORIC ACID.	The same as in NO. 26.	XXXIII. OXIDE OF SILVER.	
The same as in NO. 15.	XXII. BORACIC ACID.	XXVIII. SUCCINIC ACID.	Acids Muriatic Oxalic Sulphuric Saccho-lactic Phosphoric Nitric Arsénic Fluoric Tartaric Citric	XXXVI. OXIDE OF COPPER.
XVII. SULPHURIC ACID.	The same as in NO. 19.	XXIX. SACCHO-LACTIC ACID.		Acids Oxalic Tartaric Muriatic Sulphuric Saccho-lactic Nitric
Barytes Strontites Potash Soda Lime Magnesia Ammonia	The same as in NO. 19.	The same as in NO. 26.		

Arsénic Phosphoric Succinic Fluoric Citric Acetic Boracic Prussic Carbonic Fixed Alkalies Ammonia	XXXIX. OXIDE OF LEAD. — Acids Sulphuric Saccho-lactic Oxalic Arsénic Tartaric Phosphoric Muriatic Nitric Fluoric Citric Acetic Boracic Prussic Carbonic Fixed Alkali	Citric Acetic Arsénic Boracic Prussic Carbonic Ammonia	Arsénic Tartaric Phosphoric Sulphuric Muriatic Nitric Fluoric Saccho-lactic Succinic Citric Acetic Prussic Carbonic Ammonia	XLIX. OXIDE OF URANIUM. — Acids Sulphuric Muriatic Nitric Phosphoric Acetic Prussic Carbonic Sulphur
XXXVII. OXIDE OF IRON. — Acids Oxalic Tartaric Sulphuric Saccho-lactic Muriatic Nitric Phosphoric Arsénic Fluoric Succinic Citric Acetic Boracic Prussic Carbonic	XL. OXIDE OF ZINC. — Acids Oxalic Sulphuric Muriatic Saccho-lactic Nitric Tartaric Phosphoric Citric Succinic Fluoric Arsénic Acetic Boracic Prussic Carbonic	XLII. OXIDE OF COBALT. — The same as in NO. 41.	XLVI. OXIDE OF ANTIMONY. — Acids Muriatic Oxalic Sulphuric Nitric Tartaric Saccho-lactic Phosphoric Citric Succinic Fluoric Arsénic Acetic Boracic Prussic Carbonic Sulphur	L. ALKOHOL. — Water Æther Volatile Oils Ammonia Fixed Alkalies Sulphur Muriates
XXXVIII. OXIDE OF TIN. — Acids Tartaric Muriatic Sulphuric Oxalic Arsénic Phosphoric Nitric Succinic Fluoric Saccho-lactic Citric Acetic Boracic Prussic Fixed Alkali Ammonia	XLI. OXIDE OF NICKEL. — Acids Oxalic Muriatic Sulphuric Tartaric Nitric Phosphoric Fluoric Saccho-lactic Succinic	XLIV. OXIDE OF ARSENIC. — Acids Muriatic Oxalic Sulphuric Nitric Tartaric Phosphoric Fluoric Saccho-lactic Succinic Citric Arsénic Acetic Prussic Ammonia	XLVII. OXIDE OF TELLURIUM. — Acids Nitric Sulphuric Sulphur Alkalies Quicksilver	LI. ÆTHER. — Alkohol Volatile Oils Water
		XLV. OXIDE OF BISMUTH. — Acids Oxalic	XLVIII. OXIDE OF TITANIUM. — Acids Sulphuric Nitric Muriatic Prussic	LII. VOLATILE OILS. — Æther Alkohol Fixed Oil Fixed Alkalies Sulphur
				LIII. FIXED OILS. — Lime Metallic Oxides Æther Volatile Oil Fixed Alkali Volatile Alkali Sulphur

TABLES OF NEUTRALIZATION OF THE ACIDS
AND THE ALKALINE BASES.

The first of these tables is that by Kirwan, referred to page 185. It shews the relative powers of the principal acids in producing neutralization of the different alkaline bases, from the quantities of the latter which equal weights of the former neutralize; and in like manner the powers of these bases (taking them in equal weights,) in neutralizing the acids. It is therefore a table of the combining quantities of these substances, though not reduced to a common standard. The numbers are not altogether correct, from the imperfections of analysis, nearly unavoidable, when these researches were first undertaken. But I insert the table as being sometimes referred to, and as deriving some interest from its connection with the history of the investigation. The first division represents the powers of the acids in equal weights in producing neutralization of the bases; 100, for example, of sulphuric acid neutralizing 121.48 of potash, 78.32 of soda, &c.; the second represents in like manner the powers of the bases in equal weights in neutralizing the acids.

The second table, that by Fischer, referred to page 137, I insert for the same reason. It is founded on the numerous experiments of Richter, and is so far reduced to a standard, that the combining weight of each substance is expressed by a specific number, the quantity of each substance in the one column neutralizing the respective quantities of the substances in the other, 525 of alumina, for example, neutralizing 427 of fluoric acid, 577 of carbonic acid, &c.; and these quantities in each denoting therefore their relative neutralizing powers, or combining weights. The numbers can only be considered as approximations to accuracy.

TABLES OF KIRWAN.

I.

100 Parts of	Potash.	Soda.	Ammonia.	Barytes.	Strontites.	Lime.	Magnesia.
Sulphuric Acid	121.48	78.32	26.05	200.	138.	70.	57.92
Nitrous Acid	117.7	75.45	40.55	178.12	116.86	55.7	47.64
Muriatic Acid	177.6	136.2	58.48	314.46	216.21	118.5	89.8
Carbonic Acid	95.1	149.6	— —	554.5	251.+	122.	50.

II.

100 Parts of	Sulphuric Acid.	Nitrous Acid.	Muriatic Acid.	Carbonic Acid.
Potash	82.48	84.96	56.5	105 almost.
Soda	127.68	155.71	75.41	66.8
Ammonia	385.8	247.82	171.	Variable.
Barytes	50.	56.	51.8	282.
Strontites	72.41	85.56	46.	43.2
Lime	143.	179.5	84.488	81.81
Magnesia	172.64	210.	111.35	200.
Alumina	150.9	— —	— —	355.

TABLE OF FISCHER.

Bases.	Acids.
Alumina,525	Fluoric, 427
Magnesia,615	Carbonic,577
Ammonia,672	Muriatic,712
Lime,793	Oxalic,755
Soda, 859	Phosphoric,979
Strontites,1329	Sulphuric, 1000
Potash,1605	Succinic,1209
Barytes,2222	Nitric,1405
	Acetic,1480
	Citric,1685
	Tartaric,1694

TABLE OF THE COMBINING QUANTITIES, OR THE WEIGHTS OF THE ATOMS OF BODIES, BY DALTON.

[The numbers in this Table are referred, as has been stated (p. 151.) to hydrogen, stating the weight of its atom at 1; and the mode of reducing them to the corresponding results in the other Tables has been explained.]

1. Oxygen.....7	45. Nitrous acid51
2. Hydrogen.....1	46. Carbonic oxide12.4
5. Azote.....5	47. Carbonic acid19.4
4. Carbone.....5.4	48. Sulphurous oxide20
5. Sulphur.....15	49. Sulphurous acid.....27
6. Phosphorus.....9	50. Sulphuric acid34
7. Gold.....140?	51. Phosphorous acid52
8. Platina.....100?	52. Phosphoric acid23
9. Silver.....100	53. Ammonia6
10. Mercury167	54. Olefiant gas6.4
11. Copper56	55. Carburetted hydrogen7.4
12. Iron50	56. Sulphuretted hydrogen14
15. Nickel25? 50?	57. Supersulphuretted hydrogen 27
14. Tin50	58. Phosphuretted hydrogen.....10
15. Lead95	59. Phosphuretted sulphur.....22
16. Zinc56	60. Superphosphuretted sulphur 51
17. Bismuth68?	61. Hydrate of potash50
18. Antimony40	62. Potassium, or hydruret of potash45
19. Arsenic42?	63. Carbonate of potash61
20. Cobalt55?	64. Hydrate of soda56
21. Manganese40?	65. Sodium, or hydruret of soda 29
22. Uranium60?	66. Carbonate of soda47
25. Tungsten56?	67. Hydrate of lime52
24. Titanium40?	68. Carbonate of lime43
25. Cerium45?	69. Sulphate of lime58
26. Potash42	70. Nitrate of lime62
27. Soda28	71. Muriate of lime46
28. Lime24	72. Hydrate of barytes76
29. Magnesia17	73. Carbonate of barytes.....87
30. Barytes68	74. Sulphate of barytes102
31. Strontites46	75. Nitrate of barytes106
32. Alumine15	76. Muriate of barytes90
33. Silix45	77. Sulphate of alumine49
34. Ittria55	78. Nitrate of alumine55
35. Glucine30	79. Muriate of alumine37
36. Zircone45	80. Alum272
37. Water8	81. Potassiuiretted silix, or glass 87
38. Fluoric acid15	82. Superpotassiuiretted silix ...129
39. Muriatic acid22	83. Potash, silix and lime135
40. Oxymuriatic acid29	84. Potash, silix and barytes...155
41. Nitrous gas12	85. Fluete of silix60
42. Nitrous oxide17	86. Subpotassiuiretted ammonia...54
43. Nitric acid19	87. Oxymuriate of olefiant gas...41
44. Oxynitric acid26	

TABLE OF CHEMICAL EQUIVALENTS BY DR WOLLASTON.

Hydrogen	1,32	Sulphuric acid (dry)	50,
Oxygen	10,00	Sulphate of Soda	89,1
Water	11,32	———— Potash	109,1
Carbon	7,54	———— Magnesia	74,6
Sulphur	20,00	———— Lime	85,5
Phosphorus	17,40	———— Strontia	119,0
Azote	17,54	———— Barytes	147,0
Muriatic Acid (dry)	34,1	———— Copper	156,6
Chlorine	44,1	———— Iron	175,8
Oxalic acid	47,0	———— Zinc	180,2
Ammonia	21,5	———— Lead	189,5
Soda,	39,1	Nitric acid (dry)	67,54
Potash	59,1	Nitrate of Soda	106,6
Magnesia,	24,6	———— Potash	126,6
Lime	35,46	———— Lime	105,0
Strontia	69,	———— Barytes	164,5
Barytes	97,	———— Lead	207,0
Iron	34,5	Muriate of Ammonia	66,9
Copper	40,	———— Soda	73,2
Zinc	41,	———— Potash	93,2
Mereury	125,5	———— Lime	69,6
Lead	129,5	———— Barytes	131,0
Silver	155,	———— Lead	175,6
Subcarb. of Ammonia	49,0	———— Silver	179,1
Subcarb. of Soda	66,6	Corrosive Sublimate	170,1
Subcarb. of Potash	86,	Calomel	296,1
Carbonate of Lime	63,	Phosphate of Lead	176,9
———— Barytes	124,5	Oxalate of Lead,	186,5
———— Lead	167,	Bin-Oxalate of Potash	153,0

Though the numbers in this table are referred to oxygen as a standard, the real measure from which the greater number of the substances are compared to each other is carbonate of lime—a compound which Dr Wollaston selected as most distinctly neutral, easy to obtain in a state of purity, and to analyse, a convenient measure for the powers of acid, and affording the most distinct expression for the comparative neutralizing powers of alkalis. It remains to explain how the standard is connected with it, and the other numbers inferred.

Carbonate of lime is a compound of lime and carbonic acid. Carbonic acid is a compound of carbon and oxygen. Supposing that oxygen is to be assumed as a standard, and expressed by 10, what is the number to be applied to carbonic acid? This follows from its composition—20 of oxygen are combined with 7.54 of carbon, forming carbonic acid; but there is another definite compound,—carbonic oxide, in which 10 of oxygen are combined with 7.54 of carbon. In this latter compound, therefore, the lowest combining quantity of

oxygen is combined with carbon, and in the other twice this quantity; hence carbon is represented by 7.54, oxygen by 10, carbonic oxide by 17.54, and carbonic acid by 27.54.

Carbonate of lime is a compound of 43.7 of carbonic acid, and 56.3 of lime; or 27.54 and 35.46. The number 27.54 representing carbonic acid, it follows therefore that lime must be represented by 35.46, and carbonate of lime by 63.

If 63 of carbonate of lime are decomposed by muriatic acid, the solid product after exposure to heat will be found to weigh 69.56. Deducting from this 35.46 of lime, the quantity in 63 of carbonate, it leaves 34.1 as the quantity of muriatic acid in combination with the lime; the quantity of this acid equivalent therefore to 27.54 of carbonic acid, and to 10 of oxygen.

The equivalent weights of the other acids may be found in a similar manner; and these being obtained, it may be found by experiment what quantities of the other bases besides lime are necessary to neutralize them; and thus the equivalent quantities of these bases may be obtained. In this manner, by prosecuting the series of combinations, the numbers assigned to all the substances in the table can be found. Dr Wollaston has added the data and authorities on which he has established the results, in his paper, (*Philosophical Transactions* 1814,) to which I refer. The scale itself, already explained, p. 155, is delineated Plate VI.

TABLE OF COMBINING QUANTITIES BY BERZELIUS

Oxygen.....	100.00	Silver.....	2688.17
Sulphur.....	201.00	Mercury.....	2531.6
Phosphorus.....	167.512	Copper.....	806.48
Muriatic radical.....	159.56	Nickel.....	755.8
Fluoric radical..	60.	Cobalt.....	752.61
Boron.....	75.275	Bismuth.....	1774.
Carbon.....	75.1	Lead.....	2597.4
Nitric radical.....	79.54	Tin.....	1470.59
Hydrogen.....	6.656	Iron.....	695.64
Arsenic.....	859.9	Zinc.....	806.45
Molybdenum.....	601.56	Manganese.....	711.575
Chromium.....	708.045	Cerium.....	1148.8
Tungsten.....	2424.24	Yttrium.....	881.66
Antimony.....	1612.96	Aluminum.....	228.025
Tellurium.....	806.48	Magnesium.....	315.46
Titanium.....	1801.	Strontium.....	1418.14
Silicium.....	216.66	Barytum.....	1709.1
Rhodium.....	1490.31	Calcium.....	510.2
Platinum.....	1206.7	Sodium... ..	579.32
Gold.....	2485.8	Potassium.....	978.0

198 TABLES OF PROPORTIONS OF GASEOUS COMPOUNDS.

As connected with the preceding subjects, the table of Gay-Lussac, shewing the simple proportions by volume, in which bodies in the gaseous form combine, may be inserted; and I have added a table on the same subject by Mr Dalton.

TABLE OF THE PROPORTIONS OF DIFFERENT COMPOUNDS WHOSE ELEMENTS ARE GASEOUS, BY GAY-LUSSAC.

Substances.	Proportions in volume.		Proportions in weight.	
Muriate of ammonia	100 gas am.	100 gas mur.	ammon. 58,55	ac. mur. 61,65
Carbonate of ammonia neutral -	100 idem	100 g. carb.	idem 28,19	ac. carb. 71,81
Sub-car. of ammonia	100 idem	50 idem	idem 43,98	idem 56,02
Fluo-borate of ammonia -	100 idem	100 g. fluob.		
Sub-fluo-borate of ammonia -	100 idem	50 idem		
Water -	100 gas hyd.	50 gas oxy.	oxy. 86,755	hyd. 13,267
Nitrous oxide gas	100 nitrog.	50 oxygen	nitrog. 65,72	oxy. 56,28
Nitric oxide gas	100 idem	100 idem	idem 46,757	idem 53,245
Nitric acid -	100 idem	200 idem	idem 50,512	idem 69,488
Nitric acid -	200 g. nitr.	100 gas oxy.	idem	idem
Nitrous acid gas	500 idem	100 idem	nitrog. 54,507	idem 65,495
Ammonia	100 nitrog.	500 hydr.	idem 81,525	hyd. 18,475
Sulphuric acid	100 sulphu- rous acid.	50 gas oxy.	sulph. 42,016	oxy. 57,984
Sulphurous acid			idem 52,085	idem 47,91
Oxymuriatic acid	500 g. mur.	100 oxygen	ac. mur. 77,65	oxy. 22,55
100 Carbonic acid gas	100 g. oxide of carbon	50 gas oxy.	carb. 27,576	oxy. 72,624
100 Carbonic acid gas		100 oxygen	idem	idem
100 Carbonic oxide	50 gas oxyg.		carb. 42,99	oxy. 57,01

TABLE OF THE PROPORTIONS OF THE CONSTITUENT PRINCIPLES OF COMPOUND GASES, BY DALTON.

Names of the compounds.	Constituent principles of 100 measures of the compound.		Constituent principles of 100 weight of the compound.	
	Measures.	Measures.		
Ammon. gas	52 azote	155. hyd.	85 azote	17 hyd.
Water	100 oxyg.	200 hyd.	87 oxy.	12.5 hyd.
Nitrous gas	46 azote	55 oxyg	42 azote	58 oxygen
Nitr. oxide	99 azote	58 oxyg	59 azote	41 oxygen
Nitric acid	180 nit. gas	100 oxy.	27 azote	75 oxygen
Nitrous acid	560 nit. gas	100 oxy.	55 azote	67 oxygen
Oxym. acid	150 mur. acid	50 oxy.	76 mur. acid	24 oxygen
Sulphs. acid	100 oxygen	sulphur	52 oxy.	48 sulphur
Sulphic. acid	100 sul. acid	50 oxy.	79½ sul. acid	20½ oxyg
Carb. oxide	47 oxy.	charcoal	55 oxy.	45 charc.
Carb. acid	100 oxy.	charcoal	72 oxy.	28 charc.
Carbur. hyd.	200 hydr.	1 part ch	27 hyd.	75 charc.
Olefiant gas	200 hydr.	2 parts ch.	15 hyd.	85 charc.
Sulph. hyd.	100 hydr.	sulphur	7 hyd.	95 sulph.
Mur. of am.	100 mur. acid	100 am. g.	65 mur. acid	55 am. gas
Carb. of am.	100 carb. acid	80 am. g.	76 carb. acid	24 am. gas
Subc. of am.	100 carb. acid	160 am. g.	61 carb. acid.	39 am. gas

BOOK II.OF REPULSION AND THE POWERS BY WHICH IT IS
PRODUCED.

HAVING stated the general doctrines relating to the Attraction which operates on the particles of matter, giving rise to chemical phenomena, we have next to consider the agencies of those forces by which repulsion is established between these particles, and their mutual attractions are counteracted or modified.

The most general cause of Repulsion is the operation of the power or principle which gives rise to the phenomena of Heat,—a power which in the language of modern chemistry has been denominated Caloric. It is diffused over all the forms and varieties of matter, is capable in every body of being diminished or increased; according to its intensity it separates the particles to greater distances, and by this agency has an important influence in chemical action.

Electricity, especially under that modification which constitutes Galvanism, appears to exert a similar agency. It establishes repulsion, and is even more powerful in counteracting chemical affinity, and in separating the elements of bodies from a state of combination. It has also an intimate relation with Caloric, or is capable of producing in high intensity the phenomena of Heat.

With both these Light is connected. Its connection with Heat has long been observed, and has even led to

the opinion entertained by some philosophers of their ultimate identity. Electricity appears likewise to have relations with Light ; for bodies subjected to the electric influence become highly luminous. Light, too, may be regarded as a repulsive agent. Its particles are mutually repellent ; it subverts chemical combinations ; and its agency perhaps depends as much on the repulsion it may communicate, as on the affinities it has been supposed to exert.

These forces having thus intimate connection, and having a strict relation in the chemical agencies they exert, may be classed together, and may be regarded as general powers producing Repulsion, and in consequence of this modifying the exertion of Chemical Attraction.

The opinion has been generally received, that they are not merely general forces, but are material substances. With regard to Light this appears to be sufficiently established ; but with regard to the others, the opinion is more doubtful. If even their materiality, however, were admitted, they are still peculiar in their characters. They are present in all bodies, or at least are capable of being transmitted through them ; they are not capable of being insulated or obtained in a separate state of existence ; no specific affinities can be ascribed to them ; nor can their particular combinations be traced. They may therefore, with sufficient propriety, and with the least assumption of hypothesis, be considered as General Powers.

CHAP. I.

OF CALORIC.

OF the sensations we experience, none are more familiar than those of Heat and Cold; and with regard to these, no fact is more familiar than that the same body applied to our organs will, at different times, excite very different degrees of sensation, or even sensations totally dissimilar; being capable, at one time, of occasioning the feeling of intense cold; after a short interval, conveying perhaps an agreeable warmth; and by another change of circumstances causing extreme heat. From this it is evident, that the power of producing these sensations does not depend upon the matter itself, which is applied to our organs; for every shade of sensation is produced, without the qualities of that matter being permanently changed. It is considered therefore as depending on the operation of a certain power or subtle principle, present in bodies, and which, according to its quantity, gives rise to the power of exciting different sensations. If the body applied contain a certain quantity of it, the sensation of heat is excited; if the quantity be diminished to a certain extent, that of cold is produced; and the intensity of either sensation is proportional to the accumulation or diminution of this principle.

Even in familiar language, this distinction is observed. If a piece of iron be made hot, we conceive that a quantity of a power or principle which we call heat has been

introduced into it ; and that the property the iron in this state has, of affecting the organs of animals in a peculiar manner, depends on the presence of this power. When the iron is left to cool, we suppose that it parts with its excess of heat ; and accordingly, we find, that after a short time, it will excite the sensation only of gentle warmth. It may be cooled farther, so as to induce the sensation of cold ; and though this was once conceived to be owing to the introduction of a positive power, opposed in its nature to that of heat, the discoveries of philosophy have, even in this point, been extended to common opinion, and the power of producing the sensation of cold is considered as depending merely on the body being farther deprived of the principle of heat.

Such is the manner in which we are to view these phenomena. There exists a principle or power, capable of being communicated to all bodies. When present to a certain extent, it occasions, in animals, the sensation of heat ; and the intensity of this varies with the quantity in which it is accumulated in the body exciting the sensation. When thus present in one body it may be transferred to another, and then the power of exciting the peculiar sensation is also transferred. In the example we have taken, the piece of iron red-hot may be deprived of its heat, by plunging it into water, and in this case the water becomes hot in its turn ; the water may equally be deprived of it, and thus the excess of power may be transferred from one body to another, in whole or in part, until an equilibrium is established.

Philosophers have further observed other effects to arise from the introduction of this power. When a body acquires the power of exciting a stronger sensation of heat, it is also expanded, or its volume is augmented in every direction. The piece of iron, for example, when hot, occupies more volume than when cold. When, therefore, any hot body is cooled, the volume is diminished, and the di-

minution or increase of expansion is greater or less according to the abstraction or addition of the power on which these effects depend.

It has, lastly, been proved, that when the expansion arising from the communication of heat is carried to a certain extent, bodies change their forms, solids becoming fluids, and fluids being converted into vapours or airs.

These effects being thus connected, have been considered as originating from the same power or principle ;—the existence of which is unquestionable, though its nature may be unknown. This principle has been distinguished by various appellations, as Fire, Heat, the Matter of Heat, or the Igneous Fluid ; terms either ambiguous, or involving some hypothesis, and which are superseded by the unexceptionable appellation of Caloric.

By Caloric, then, is to be understood a power present in bodies, the cause of their expansion and of their existence in the fluid and aëriform states ; and which, when present in a certain quantity, excites in animals the sensation of heat, the sensation of cold being the effect of its abstraction.

Respecting the nature of this power, different opinions have been entertained : some have considered it as a subtle fluid, diffused over matter, and capable of entering in greater or less quantity into every body : others have supposed all the phenomena exhibited by heated bodies to arise from a peculiar state of these bodies,—a vibratory motion, more or less violent, of their minute particles. It would be improper, on entering on the consideration of Caloric, to engage in the discussion of this question, since it can only be determined from a full knowledge of the properties of this power, and its relations to other matter. Nor is any such preliminary discussion necessary, since whatever may be the nature of the power which the term Caloric expresses, its existence is sufficiently demonstrated, as the cause of certain effects ; and although the nature of

that cause may be unknown, the effects themselves, their relations to each other, and the general laws according to which they are produced, may be investigated with sufficient precision.

I shall deliver the history of Caloric under the following sections. In the first, I may facilitate the prosecution of the subject, by taking a general view of the distribution of this power; in the second, I shall consider its effects on matter; in the third, the laws of its communication and propagation; in the fourth, the comparative quantities of it which bodies contain; in the fifth, the comparative quantities which the same body, in different forms, contains; under the sixth, may be reviewed the opinions which have been advanced with regard to its nature; and its chemical history may be concluded, with an enumeration of the causes by which its equilibrium is subverted, or heat and cold produced, and the applications of these to practical chemistry.

SECT. I.—*Of the Distribution of Caloric, the Production of Temperature, and the methods of measuring it.*

THE state of a body with respect to its power of producing the different effects arising from the presence of caloric, is termed its *Temperature*. In each body the temperature depends on the quantity of caloric which it contains. If at any temperature it contain a certain quantity, the addition of caloric to it raises the temperature; in other words, the body now possesses the power of exciting either a weaker sensation of cold, or a stronger sensation of heat, and of producing in other bodies to which it may be applied, a greater degree of expansion.

Of those effects, by which temperature is estimated, that of exciting the sensation is so limited, and so much influenced by the state of the sentient organ, as well as by other circumstances, that it does not afford any accurate indication.

Expansion is an effect of caloric more regular and extensive, and is therefore now always employed to measure temperature. When two bodies produce the same increase or diminution of volume in a third body, to which they are equally applied, they are said to be at the same temperature; and any body is said to be at a higher or lower temperature, as it produces a greater or less expansion in another body with which it is in contact.

An instrument has been contrived, by which the degrees of expansion can be accurately measured, and which is of the first importance in all our experiments on the subject of caloric. This instrument, named the *Thermometer*, is of modern invention: the honour of it is due to Sanctorius, an Italian physician, who lived in the 17th century. The expansion which air suffers when it is heated, it occurred to him might be used as a measure of the

variations of heat. He employed for this purpose a hollow glass ball, with a long cylindrical tube, open at the extremity, placed vertically, the ball being uppermost. A small quantity of the air being expelled, by applying heat to the ball, the open end of the inverted tube is immersed in a coloured liquor, and as the air in the ball cools, the fluid rises. A scale of equal parts being applied to the tube, the extent of the expansion of the included air by heat is accurately discovered by the descent of the coloured liquor, its condensation by cold being marked by its ascent. Fig. 40. Plate IV. represents the common air thermometer.

An important improvement, by which the thermometer was rendered much more accurate and manageable, was made by the members of the Academy del Cimento, by substituting a liquid as the measure of expansion, and inclosing it in a tube hermetically sealed. Spirit of wine coloured was the liquid that was first employed. Mercury was afterwards used by Halley, and oil by Newton. The two former are in use, the last is seldom employed.

The thermometer constructed with either fluid, is merely a glass ball, with a long tube issuing from it, of a very small bore, and perfectly cylindrical, the ball being entirely, and the stem partly filled with mercury or with coloured spirit. This is done by heating the ball so as to expel the greater part of the air it contains; it is then allowed to cool, the end of the tube being immersed in the liquid with which the thermometer is designed to be constructed; a portion of this liquid rises into the ball; it is then boiled in it, the air is expelled, and its place is supplied by the vapour. As this condenses from cooling, a fresh quantity of the liquid in which the tube is immersed rises in it, and the operation is repeated, until the whole of the air is expelled, and the ball and part of the tube are filled with the thermometric liquid. The end of the tube is then melted and closed.

The principle on which the thermometer indicates tem-

perature, is, that caloric has a tendency always to preserve an equilibrium; so that if two bodies, at different temperatures, be brought into contact, it will pass from the one at the higher into that at the lower temperature, until the temperature of both is the same. When the thermometer, therefore, is applied to a hot body, it receives caloric; when to a cold one, it communicates part of its own caloric; and this communication of caloric from the one to the other continues until both the instrument and the body to which it is applied arrive at an equality of temperature. Now, the temperature of the thermometer is discovered from the volume the thermometrical fluid occupies in the instrument. When its temperature is raised, the fluid is expanded, and of course rises in the tube: when its temperature is reduced, it is contracted and descends; the changes of volume being accurately measured by a graduated scale attached to the tube. The point at which the fluid becomes stationary indicates its temperature; and, from the property of caloric, just stated, this indicates the temperature of the matter with which the thermometer is in contact. The instrument is made with a small ball, and with a tube of a very fine bore, that it may indicate changes of temperature more speedily and with more accuracy.

It is obvious, that, strictly speaking, the observed changes of volume in the thermometrical fluid are not the real changes; for the glass ball is expanded by heat, and contracted by cold, and, in the one case, must render the expansions apparently less than they really are, and in the other must diminish the contractions. Hence it is only the excess of the expansion or contraction of the fluid above that of the glass, that is observed. From the principle, however, on which the scale is constructed, this does not introduce any material error.

The fluid in thermometers is either mercury or coloured spirit, and to certain purposes one is better adapted than the other. The mercurial is superior in accuracy to

the spirit thermometer; the expansions of mercury, from given alterations of temperature, being more uniform than those of alkohol. It also suffers changes of temperature with more celerity, and is therefore more sensible; and to suffer any given alteration of temperature, it requires less caloric than the other. It can also measure higher temperatures, pure vinous spirit or alkohol being converted into vapour at 182° of Fahrenheit; while mercury is not converted into vapour under 650° . Alkohol, however, has the advantage of being capable of measuring very low temperatures, mercury becoming solid at 39° below 0 of Fahrenheit, while alkohol not freezing can be employed to measure the most intense colds. Its changes of volume are also more regular at these low than they are at high temperatures. At all temperatures too, at which it is practicable to apply it, its expansions from given changes of temperature are greater than those of other fluids; hence the changes in the thermometrical scale constructed with it are more conspicuous; but, at the same time, as its expansibility very sensibly augments with its temperature, they are less accurate, and the ratio of expansibility varying, too, with its concentration, another source of error is introduced. The degree of expansion can be rendered as apparent with quicksilver, by using a tube of a very fine bore, while in alkohol this cannot be done to the same extent, from the difficulty occasioned by its adhesion to the tube. On the whole, therefore, for every purpose except that of measuring very low temperatures, the mercurial should be preferred to the spirit thermometer. Oil has scarcely any advantage as a thermometrical fluid, and its viscosity causes it to adhere more or less to the tube.

The air thermometer has the advantage of indicating very minute changes of temperature, air being so greatly altered in its volume by alterations of temperature, and on this account it is occasionally used with advantage for some purposes. In other respects it is very imperfect, incon-

venient from its form, liable to variations from changes in the pressure of the atmosphere, and inapplicable to the measurement of any extensive range of temperature. The form is improved, by using a ball with an upright stem curved, so that the liquid in the stem confines the air in the ball, as is represented fig. 41. And a more important modification of it is the Differential Thermometer of Mr Leslie, which consists of two air thermometers, their stems being joined by a common tube, as represented fig. 42. A portion of coloured liquid, (sulphuric acid tinged with carmine,) is introduced before the tube is hermetically sealed, so as to fill the curvature and a certain portion of each stem. This liquid is equally acted on by the elasticity of the air in each ball; and as this is equally affected by any variation of the temperature of the surrounding medium, the liquor remains stationary. But if one of the balls be exposed to any heating or cooling cause, the increased or diminished elasticity of the air in this ball causes the liquid in its stem to be depressed or raised, and thus indicates the change. A scale is attached, which Mr Leslie has formed by dividing the interval between freezing and boiling water into 100 degrees, and subdividing each of these decimally, these last divisions being the degrees. The instrument being hermetically sealed, is not affected by any variations of atmospheric pressure. It is peculiarly applicable to some subjects of investigation, to be afterwards noticed. A variation rendering it more convenient in form, by Dr De Butts of Baltimore, is represented fig. 43. It is a straight tube, with a ball at the top, inserted in another short tube with a ball at the bottom: the under ball contains a small portion of sulphuric acid tinged, in which the extremity of the upper tube is immersed; the joining is hermetically sealed, and the liquor in the long tube is adjusted by the relative quantities of air in the two balls.

It is of importance, more particularly in meteorological

observations, to have a Register Thermometer, which shall mark the maximum and minimum of temperature that has occurred, during any interval between the times of observation. Two instruments of this kind are in use, one invented by Six *, the other by Rutherford †. The former consists of a curved tube or inverted syphon terminated at one extremity, with a long cylindrical bulb filled with spirit of wine, and usually recurved, for convenience of construction, so as to be parallel with the other. The curved tube contains a column of mercury, which rises to about one half of the height in each leg, and above this is spirit of wine, connected of course in the one leg with the spirit in the bulb, and in the other filling the tube, which at this end has a small bulb containing air, to admit of the movement of the whole column from the variations of temperature. On the surface of the column of mercury, in each tube, is a small float of glass, including a steel wire with a weak spring, so that when it is pushed on by the movement of the quicksilver, it does not return, but remains stationary at the farthest point to which it had advanced; it thus indicates in the one tube, that with the small bulb partially filled, the greatest heat; and in the other, the greatest cold. When the instrument is to be rectified for a new observation, the floats are brought down to the mercury by applying a magnet to the outside. In Rutherford's thermometer, a small cylinder of steel is included in a common mercurial thermometer, of such a size that it moves in the tube; it rests on the column of mercury, and the instrument is laid horizontally: when the mercury advances from rise of temperature, the steel index is pushed forward, but it does not return when the mercury falls back; hence the point at which it remains indicates the highest temperature that has taken place: it is rectified by raising the thermometer so as to allow it to fall down.

* Philosoph. Transact. vol. lxxii, lxxii. † Edin. Transact. vol. iii.

To mark the greatest cold a spirit thermometer is used, having a small conical piece of coloured glass with its point towards the bulb, of such a size as to move easily, yet nearly fill the calibre. When in the horizontal position, with this index immersed at the end of the column of spirit, on the spirit contracting from cold and receding to the bulb, the index from the influence of adhesion at the surface is carried with it; but if the temperature rise, the spirit advancing passes it, and leaves it stationary at the lowest point to which it had descended. It is rectified by raising the thermometer with its bulb uppermost, so that the float falls to the bottom of the column. And if the two thermometers be placed on one frame, with their bulbs at the opposite extremities of it, they are both rectified by the same movement. To these instruments the common scale is attached. That of Rutherford's is preferable, as in the other it is often difficult to bring down the floats.

To render the thermometer an instrument of any value, two points were necessary to be attained: *first*, that it should be so constructed, as that the indications by different instruments should correspond; and, *secondly*, that the just relation should exist in the indications of the same instrument at different temperatures. Both these points have occupied much attention.

First, For some time after the invention of the thermometer a great difficulty was experienced in constructing the scale, so that the observations made with one instrument might correspond with those from another. Different methods were employed. The first attempt seems to have been to construct the degrees of the scale on the stem according to proportional parts, by which the fluid in the bulb would be expanded by certain increments of heat from a fixed temperature, such as that of melting ice. On this principle, Newton constructed a scale, supposing the fluid in the bulb to be equal to 10,000 equal parts at the temperature of melting ice, and the rise in the tube to be

denoted by a certain number of parts, from an augmentation to certain fixed temperatures. The scale of Reaumur appears to have been founded on the same principle. The method, however, is not susceptible of sufficient precision. Another, which was afterwards introduced, and which is the one now in use, is that of employing two fixed points of temperature, and dividing the interval into an equal number of parts. This seems to have been suggested by Newton. It had been known that water freezes or ice melts always at one uniform temperature. If we immerse the thermometer in melting snow or ice, the fluid within will fall to a certain part of the tube, where it will stop, and, however long we allow it to remain, it will descend no lower. And the experiment, if repeated at any time, will afford the same result, the fluid always standing at the same part. If, therefore, we mark this, we obtain one fixed point, which must be the same in every thermometer. It had been observed by Hooke and by Amontons, that under the medium pressure of the atmosphere, water boils at one uniform temperature. If, therefore, under such a pressure, the thermometer be immersed in boiling water, the height to which the mercury rises in the tube will be uniform, and this being marked, will afford another invariable point. These two, then, the point at which water freezes, and that at which it boils, may be connected by a scale divided into any number of equal degrees; and thus, whatever may be the length of the tube, or its diameter, the degrees marked upon it will correspond with those marked on any other according to the same scale. The scale has been different in different countries; but when two points are thus fixed, which in all correspond to certain numbers, whatever names may be given to these numbers, or whatever may be the number of parts intermediate between these points, it is easy, by calculation, to bring them to correspond. The scale is prolonged by similar degrees, descending from the freezing point of water, so as to denote lower tempera-

tures, and ascending from that of boiling water to express higher temperatures*.

The thermometer commonly used in this country is one first made by Fahrenheit, a German artist, and thence known under his name. The lowest temperature marked upon its scale is that produced by a mixture of snow and sea-salt, this being the lowest temperature known in Fahrenheit's time †. The range of temperature between it and the freezing point of water, he divided into 32 parts or degrees, and commencing the numeration at the lower temperature, the freezing point of water came to be at the 32d degree. He assumed another fixed temperature, that of the heat of the human body, (found by placing the bulb of the thermometer in the mouth,) at 64 above the freezing of water, or 96 from the commencement of the scale. The interval between the freezing and boiling points of water is found to be equal to 180 parts or degrees. The boiling point is therefore 212°. The peculiar construction of Fahrenheit's scale seems to have originated in the circumstance, that the thermometer was at first valued as an instrument capable of giving indications of natural tempera-

* In the principles of Chemistry, by Nicholson, is an excellent account of the details with regard to the construction and graduation of thermometers. De Luc in his Researches on the Modifications of the Atmosphere has entered very fully into the history of the thermometer; and some just observations on the graduation of the instrument, particularly with regard to the necessity of the stem as well as the bulb being heated, are made by Mr Cavendish, (*Philosophical Transactions*, vol. lxxvii.), and by Dr Crawford in his Treatise on Heat.

† Fahrenheit does not seem to have taken his lower temperature with much precision, as he speaks of a mixture of snow with sea-salt, or sal ammoniac; and from such a mixture, the temperature is 4°, or 6° below the beginning of his scale. *Philosophical Transactions*, vol. lxxviii, p. 304.

tures; and more particularly, as Fahrenheit himself remarks, in reference to meteorological observations. Commencing, therefore, with the greatest cold known at that time, he raised the scale to what was supposed to be the greatest natural heat, that of blood heat, or the temperature of the human body. This he fixed at 96° , as a convenient number, capable of affording intermediate terms by bisection. The interval between the commencement of the scale and the freezing point of water included, according to this numeration, 32 degrees; and afterwards, in prolonging the scale, the temperature of boiling water was found to be 212° .

In France, the thermometer named Reaumur's was formerly employed. In it the scale commences at the freezing point of water, which is therefore marked 0, or what is named Zero. The space between it and the boiling point of water is divided into 80 degrees, the point at which water boils being termed the 80th degree. The peculiarity of Reaumur's scale appears to have arisen from the principle on which it was constructed. He supposed the liquid in the bulb (weak spirit of wine) equal to 1000 parts at the temperature of freezing water, and the increase of volume to be equal to 80 parts, when heated to the point at which water boils. Hence the latter temperature was denoted by this number.

The correspondence between these two thermometers is easily found, by the following general formula: Each degree of Fahrenheit's scale is equal to $\frac{4}{9}$ ths of a degree of Reaumur's. If, therefore, the number of degrees of Fahrenheit's, either above or below the freezing point of water, be multiplied by 4, and divided by 9, the quotient will be the corresponding number on Reaumur's. Or, to reduce those of Reaumur's to Fahrenheit's, they must be multiplied by 9 and divided by 4, the quotient will give the number of degrees of Fahrenheit above or below the freezing point of water; and as that point is marked on

that scale 32, this number, if the degrees are above, must be added to the quotient to give the corresponding number on Fahrenheit's; if they are below it the quotient is to be subtracted from 32.

Besides these, there have been other divisions of the thermometrical scale *. That of De Lisle's was founded on the contraction of mercury in cooling from the boiling to the freezing point of water. Taking the original volume at 10,000, the contractions were supposed to be 150. The scale commenced, therefore, at the boiling point of water, and proceeded to the freezing point through 150 degrees. The division of Celsius, which was used in Sweden, has been revived in France, as being conformable to the new system of measures, and affording in itself the most simple and natural division. It commences at the freezing point of water, and between that and the boiling point is divided into 100 parts; hence it has been named the Centigrade Thermometer. Each degree of Fahrenheit's scale is equal to $\frac{5}{9}$ ths of a degree of the centigrade scale. To reduce, therefore, the degrees of the former to those of the latter, the same formula is to be used as in the preceding paragraph, multiplying only by 5, and dividing by 9. Or, to reduce those of the centigrade scale to Fahrenheit's, their number must be multiplied by 9, and divided by 5. Tables of correspondence exhibit the results more directly, and I therefore insert them at the end of the chapter.

Of these scales, the Centigrade has been supposed to be the preferable division; it is superior in every respect to that of Reaumur's, and is more simple than Fahrenheit's. Fahrenheit's, however, has two important advantages, which give it a decided preference;—one is, that its divisions are smaller, and hence observations with it are more minute, without the necessity of using fractional parts,

* See Martine on Heat and Thermometers.

which, in observations, are liable to be neglected, and in calculation are inconvenient; the other, that the commencement of the scale being placed at a low temperature, we have seldom to express negative degrees; while, in the centigrade, and in Reaumur's scale, it is always necessary, either by prefixing the signs of *plus* and *minus*, or by terms, to denote whether the number stated is above or below the zero. Yet Fahrenheit's is a very arbitrary and inartificial division. A scale preferable to any of these might be formed, by taking, as the extreme points, the temperatures of freezing and boiling quicksilver; the one being -39° of Fahrenheit, and the other $+655^{\circ}$ *, and dividing the intermediate space into 1000 parts. The degrees would thus be smaller than Fahrenheit's, without being too much so, to be inconvenient either in the construction of the instrument, or for observation; and the commencement of the numeration being so low, we should scarcely ever have to express negative degrees. The commencement of the scale would also be about the lowest natural temperature. It seems the most natural method, too, to assume the freezing and boiling points of the fluid, which is the most accurate thermometrical one, as the fixed points of the scale which its expansions are to measure. These points, by careful experiment, might be fixed with accuracy, and the degrees which correspond with the freezing and boiling points of water determined by actual trial; and this being done, in the construction of the instrument the common method might still be followed, though the scale might be divided and numbered in relation to the freezing and boiling points of quicksilver. Assuming the freezing and boiling points of quicksilver to be according to Fahrenheit's scale -40 , and $+655$, the freezing and boiling points of water are 99 and 347 on this new scale.

* This is the number stated by Crichton; by Dalton it is stated at 660, and by Irvine at 672.

Secondly, Another point not less necessary to be attained in the construction of the thermometer, is, that the real relations shall exist between the indications of the instrument and the respective temperatures; in other words, that the expansion and contraction of the thermometrical fluid correspond accurately with the real increments and decrements of temperature. If a thermometric liquid from a given augmentation of temperature, suppose 10 degrees, expand more at one part of the scale than at another, then the indications from its changes of volume cannot be accurate; because its scale being of equal parts, a given number of these parts, where the expansion is greater, will indicate a greater rise of temperature than has been produced.

The general form of experiment to determine this, executed at different times by Halley, Brooke Taylor, and others, consisted in selecting a thermometer having a tube perfectly cylindrical, immersing it in hot water, and marking the point at which the thermometrical fluid stands; then immersing it in an equal weight of cold water, and again marking the part of the scale where it is stationary; lastly, mixing the two portions of water, and observing at what point the fluid of the thermometer immersed in the mixture stands. If the temperature indicated be the exact mean between the two temperatures, it may be concluded, that the expansions proceed equally, and, of course, that the indications will be correct; while, if it differ from the mean, it must be concluded that the ratio of expansion is unequal. The experiment requires much care in the execution to guard against sources of error, particularly from the effect of the vessel on the temperature of the mixed fluid, and the abstraction of heat by the air, or by the escape of vapour. It was executed with much attention by De Luc, at an early period; and the result was, that the different thermometrical fluids do not expand in an uniform proportion to the quantities of caloric they receive, but proceed in an increasing ratio as the temperature is raised.

Quicksilver was the most regular; yet even in it the deviation was apparent. When a quantity of water at 45° was mixed with an equal weight at 200.7° , the mercurial thermometer in the mixed fluid indicated the temperature to be 2.5 degrees less than the arithmetical mean; and when the experiment was made at other temperatures, corresponding results were obtained *. With other fluids the deviations were greater. While the mercurial thermometer, placed in water of the precise mean temperature between 32° and 212° , instead of indicating that mean 122° stood at 119° ; a thermometer with olive or linseed oil indicated only 117° , one with alcohol 108° ; and so great was the irregularity in water, that its indication was only 75° . Hence the superiority, in accuracy, of the mercurial thermometer.

It follows, however, from the deviation from equality in the expansions even of quicksilver, that the thermometer constructed with it cannot, according to the common division of the scale, be considered as an exact measure of temperature. The error indeed is less than it otherwise would be, owing to the mode in which the scale is formed; for the two fixed points, the freezing and boiling points of water, being found by actual experiment, the amount of the error, from the progressive expansion between these, is divided among the intermediate degrees. It is of course greatest at the mean degree; here, according to De Luc's estimate, it is equal to 3 degrees; so that when a common thermometer indicates a temperature, as 119° , the real temperature is 122° . This might be obviated, by accommodating the degrees to the real expansions; and in delicate investigations on temperature, if the fact were absolutely certain, a thermometer on this construction ought to be employed. In the common construction of the instrument

* Recherches sur les Modifications de l'Atmosphere, tom. i, p. 298. 302.

it is not attended to; and hence has been proposed a table which shall point out the correspondence between the apparent and the real indications. De Luc has given one from the above experiments, adapted to Reaumur's scale, to which I have added the corresponding numbers on the scale of Fahrenheit. The first column, according to each scale, expresses the temperatures on the mercurial thermometer, graduated in the common manner, and the second the corresponding real temperatures.

Reaum.	Reaum.	Fahr.	Fahr.
80	80.	212.	212.
75	75.28	200.75	201.38
70	70.56	189.5	190.76
65	65.77	178.25	179.93
60	60.96	167.	169.16
55	56.15	155.75	150.34
50	51.26	144.5	147.33
45	46.37	133.25	136.33
40	41.40	122.	125.15
35	36.40	110.75	113.90
30	31.32	99.5	102.47
25	26.22	88.25	90.99
20	21.12	77.	79.52
15	15.94	65.75	67.86
10	10.74	54.5	56.16
5	5.43	43.25	44.22
0	0	32.	32. *

Dr Crawford, to whom, in his researches on heat, the determination of this point was of primary importance, repeated these experiments, with much attention to accuracy. He found, that the mercurial thermometer indicated less than the mean temperature, but the deviation was not so great as in the experiments of De Luc, being, on an average, little more than 0.5 of a degree, when the difference of temperature between the two portions of water amounted to 100 degrees †; and according to a cor-

* Recherches, t. i, p. 309.

† Experiments on Animal Heat, p. 22, &c.

rection he afterwards made of an error in the calculation not more than 0.25° *.

This result was confirmed by an experiment made in a different manner. A mercurial thermometer was suspended in an apparatus, in which it was equally exposed to the influence of air, cooled by snow to 32° , and of air heated by watery vapour to 212° . It rose to 121° , and remained stationary at that for fifteen minutes, the time during which the experiment was continued. It indicated, therefore, a temperature one degree inferior to the arithmetical mean, when the difference of temperature amounted to 180 degrees †, which agrees nearly with the result of the preceding experiment. Even this deviation from the precise mean he supposed to be diminished, by admitting a correction for the effect of the temperature on the fluid in the stem of the thermometer ‡.

* Experiments, &c. p. 488. † Ibid. p. 40. ‡ Ibid. p. 48.

De Luc had observed, that the experiment of determining the accuracy of the thermometer, by mixing equal portions of hot and cold water, and observing the temperature indicated, is conclusive only on the assumption, that the capacity of water for caloric is permanent within the range of temperature operated on, while there is every probability that it is increased. The capacity for caloric is connected to a certain extent with the volume a body occupies. Now, the expansion of water proceeding in an increasing ratio, the volume, when two equal portions at different temperatures are mixed together, must be below the mean; there is accordingly, in mixing equal portions of water at 32° and 212° , a condensation of volume equal to about 1.90th of its bulk. This is probably accompanied with a diminution of capacity, and from this cause a quantity of heat must be given out, which must raise the temperature above the true mean. The extent of this, however, cannot be considerable. It was to obviate this objection that Dr Crawford made the experiment, stated in the text, of exposing the thermometer equally to the influence of air cooled by snow to 32° , and

The deviation therefore of the mercurial thermometer from perfect accuracy appears in these experiments to be less than that stated by De Luc; and the latter philosopher admitted even, from some considerations, that it might be less than appeared in his experiments. It is perhaps underrated however by Crawford. Above 212, the irregularities in the expansions of mercury become greater; and, in other liquids are so considerable, as to render them unfit to measure temperature with accuracy. The inaccuracy, in all these cases, arises from the expansibility of fluids, augmenting as their temperature is raised; and to render the thermometer a correct measure of temperature, its degrees ought to be adjusted to this. Hence the *desideratum* that this should be ascertained*.

Another method of determination has been lately employed by Petit and Dulong,—that of comparing the expan-

of air heated by steam to 212°; and from this principally he inferred, that this instrument is an accurate measure of heat; and also inferred, combined with the other mode of experiment, that the capacity of water for caloric scarcely varies from 32° to 212°.—(Treatise on Animal Heat, p. 39. 61.)

* Mr Dalton has inferred, that the deviation from accuracy in the common mercurial thermometer is much greater than is believed. The apparently equal expansion of mercury, he supposes to arise from our taking a small portion of the scale of expansion, and this at some distance from the freezing point of the liquid; but its real expansion, as well as that of all pure homogeneous liquids, is, he infers, as the square of the temperature from their respective freezing points, or points of greatest density; and according to this, the deviations are very considerable. He has given a table representing this. This law of expansion seems, however, to rest rather on analogy than on experimental evidence, and cannot be regarded as established. Dr Young has remarked, that it does not appear to hold true either with mercury or with alkohol, and not even exactly with water.

sions of the mercurial thermometer with the expansion of a homogeneous body of such a nature that the circumstances which influence expansion shall have no influence on it. Such a body, they remark, must evidently be taken either from among the gases, or from among solids which are of great infusibility. Experiments prove that all the gases expand the same from the same increase of temperature; it is natural therefore to conclude, that the expansion in each is uniform, and that of course equal enlargements of volume correspond with equal increments of temperature. On this principle Gay-Lussac inferred that the mercurial thermometer is regular between the temperatures of freezing and boiling water. The expansions of solids, which are of very difficult fusibility, have been inferred to be uniform; and, in particular, those of the metals appear, from the experiments of Lavoisier and Laplace, to be so between these temperatures. But if bodies so different as the metals and the gases observe the same law in their expansions, it becomes extremely probable that these expansions indicate the real temperatures. On this principle Petit and Dulong instituted a comparison between the expansions of gases and of solids with the mercurial thermometer in elevated temperatures. With regard to the correspondence in the dilatations of air with the indications of the mercurial thermometer, they obtained the following results *.

Temperatures indicated by the Centigrade Scale.	Temperatures indicated by the dilatation of air.	Differences.
100°	100	0
150	148.70	1.30
200	197.05	2.95
250	244.17	5.83
300	291.77	8.23

* Ann. de Chim. et Phys. t. ii. p. 240. Ph. Mag. vol. xlviii.

Other results, obtained by a variation in the mode of conducting the experiment, were nearly the same. It follows, that the expansion of mercury in the thermometer increases progressively above that of air; so that if the latter be regarded as uniform, and of course as an exact measure of temperature, it must be concluded that the indications of the mercurial thermometer are too high compared with the real temperatures, and this more especially from the mode of construction of its scale above the heat of boiling water. They next submitted to comparison the expansions of the mercurial thermometer and the expansions of the metals at elevated temperatures, employing for this purpose an instrument constructed of a compound bar of platina and copper, capable of shewing with much precision the difference of expansion in the two metals in a given elevation of temperature. The results in this method were altogether the reverse of those in the former. The expansion of the metals exceeded progressively that of the mercurial thermometer, so that the temperature of 300, as indicated by the latter, corresponded with that of 310 as indicated by the former. Hence, taking an air thermometer, a mercurial thermometer, and a solid metallic thermometer, the temperature indicated by the first, as 300° , would by the second be 310° , and by the third 320° . The progressive expansion of glass they found to exceed even that of metals. The whole investigation, it is obvious, remains in some measure indecisive; for there is no absolute proof which of the propositions involved in it is true. Petit and Dulong consider it as most probable that the expansion of gases is uniform, proportional to the temperature; hence the indications of the mercurial thermometer must exceed those of the real temperature, and this to a greater extent as the temperature is higher; and the deviations would be greater than they appear, were it not that the expansion of glass still more exceeds the regular expansion, and

hence produces in the thermometer, by the effect of the expansion of the bulb of the instrument on the contained fluid, a compensation to a certain extent for the increasing expansion of the latter.

The increasing expansion of the glass, however, if it exceed a certain amount, may itself prove a source of error in the construction of the thermometer, and must do so if the expansions of the thermometrical fluid are really equable. It is obvious that in raising the temperature of the thermometer, the whole expansion of the contained fluid is not shewn. The glass ball being expanded admits so far of the expansion of the fluid, and it is the excess only of the expansion of the latter over that of the former that appears by the rise in the stem. If the expansion of the glass were equable, this would cause no error, but if otherwise it must do so : if decreasing, it must render the apparent expansions of the mercury as the temperature rises progressively greater than they actually are ; if increasing the reverse. Now the fact on all those points, as well as in the regularity of expansion in quicksilver itself, is still somewhat doubtful, and there is not much probability, even on the assumption of their being an adjustment such as has been supposed, that it will be such as to obviate all error. At the same time, from the small effect which can arise from any increasing expansion of the glass, within even a considerable range of temperature, the error it will give rise to cannot be great ; and if it exceed that of the mercury, it may even render the indications more accurate.

The thermometer, on the construction hitherto described, is necessarily limited in its application. When made with alcohol, it can be used, indeed, to measure the most intense colds. . But it cannot, even with mercury, the least volatile liquid, be applied to indicate very high temperatures, as the fluid must be converted into vapour, and burst the tube.

To supply this deficiency, various methods have been proposed. A very ingenious one was employed by Newton. Assuming that the quantities of heat lost by a body, in small portions of time, are proportional to the excess of its temperature above that of the surrounding medium; or that, taking the times of cooling in arithmetical progression, the decrements of heat will be in a geometrical one; he concluded, that from observing the time of cooling, until the temperature is sufficiently reduced to admit of being accurately measured in some other mode, the original temperature may be discovered. The method he followed was to raise a mass of iron to a red heat, remove it from the fire, and suspend it in the air. He then placed on its surface different fusible substances, and observed the times at which, in the progress of the cooling, they became solid. And as he had previously found, by an oil thermometer, the temperature at which tin melts, this enabled him to calculate all the other temperatures, according to the same thermometer, up to the point at which the observations had commenced. By this method, he determined various high temperatures, such as that of ignition visible in the dark, which he stated at 635° of Fahrenheit, and in day-light at 1000° . It was afterwards applied by Irvine, as well as by Crawford, in their delicate experiments on the absolute heats of bodies, this being the only mode in which they could determine, with any accuracy, the quantities of heat lost by bodies mixed together at different temperatures, during the short time which elapses before a common temperature is formed *. The method itself, as applied to measure high temperatures, appears to be liable to some errors, as its results do not agree precisely with those determined by other modes, the accuracy of which is rendered probable by their coincidence. The errors arise probably from the difficulty

* Crawford on Animal Heat, p. 99.

of noting, with perfect exactitude, the times at which bodies melt or congeal; a little deviation from the real time giving rise to a considerable error in the estimate of the temperature, particularly in the higher parts of the scale.

Biot has proposed another method *, founded on the rate of progression of temperature through a metallic bar exposed at one extremity to a constant source of heat. This being found by means of thermometers, the bulbs of which are placed in cavities in the bar at certain distances, through a certain interval distant from the more intense heat, the latter may be inferred from it. The method is an ingenious one; but the influence of the air, the difficulty of adjusting the distances and the temperatures, and that of rendering uniform the extreme heat, must render it scarcely susceptible of much precision.

Different instruments (named Pyrometers, as being applied to measure great heats) have also been invented; of the greater number of which, it is scarcely necessary to give a detailed account. The difficulty of contriving an unexceptionable instrument of this kind has arisen partly from the difficulty of finding a substance not liable to be altered by a high temperature, and which shall suffer a change of volume sufficiently perceptible to be accurately measured; and partly from that of finding a measure, which shall not be affected by the high temperature, and be at the same time sufficiently delicate.

The pyrometer which has come into most general use is that invented by Mr Wedgwood. The pure earth named Alumina, and the earthy mixtures (the clays) in which it predominates, have the property of contracting instead of expanding by heat. This contraction becomes evident, when the clay is raised to a red heat; it continues

* Journal des Mines, t. xvii. 203.

to proceed until it vitrifies, and the total contraction in pure clays exceeds considerably one-fourth of the volume. It occurred to Wedgwood, that from this property it might be employed in the construction of a pyrometer. The contraction the clay suffers is permanent, or it does not return to its former dimensions when cold : the degree of contraction, therefore, can be ascertained without any fallacy from the existing temperature, and will indicate the extreme of temperature to which it has been exposed.

This pyrometer consists of a gage, composed of two straight pieces of brass, twenty-four inches long, divided into inches and tenths, and fixed on a brass plate, so as to converge ; the space between them at the one extremity being five-tenths of an inch, and at the other three-tenths. The clay well washed is kneaded, and fashioned into small cylinders, flattened on one side, made in a mould, so as to be adapted exactly to the wider end, after having been heated to redness. It is evident, that in exposing one of these pieces to a high temperature, the contraction it has suffered may be measured, by the length to which it can be slid into the converging groove *.

To add to the utility of this instrument, by connecting it with the mercurial thermometer, and by ascertaining the proportion between the degrees of each, Mr Wedgwood made a series of experiments. The scale of his pyrometer commences at red-heat visible in day-light. The mercurial thermometer cannot easily measure any temperature above 500° or 550°. To measure the interval between the termination of the scale in the one and its commencement in the other, he employed the expansions of a square piece of silver, measured in a gage of earthenware, constructed in the same way as his pyrometer ; and by the same method, he found out the proportion between

* Philosophical Transactions, vol. lxxii, p. 310.

each degree of his scale, and the usual thermometrical scales. Each degree of his pyrometer he found to be equal to 130° of Fahrenheit. The commencement of his scale, or the point marked 0, corresponds with $1077\frac{1}{2}^{\circ}$ of Fahrenheit's scale. Hence it is easy to reduce either to the other, through their whole range. The scale of Wedgwood includes an extent of temperature equal to about $32,000^{\circ}$ of Fahrenheit, or 54 times as much as that between the freezing and boiling points of mercury *. Its commencement is at $1077\frac{1}{2}^{\circ}$ of Fahrenheit, or red-heat visible in day-light; its extremity is 240° ; but the highest heat that he measured with it is 160° , or $21,877^{\circ}$ of Fahrenheit; this being the temperature of a small air furnace, and 30° of the scale above the point at which cast-iron melts. Guyton has more lately affirmed, that the relation which Mr Wedgwood assigned to the degrees in his scale and those of the usual thermometrical scales is altogether incorrect. Instead of each degree being equal to 130° of Fahrenheit's scale, it is equal only to 62.5: instead of 1077 of Fahrenheit, corresponding with the commencement of Wedgwood's, 517 is the corresponding number; and of course all the higher parts of the pyrometrical scale indicate thermometrical degrees by far too great; the heat of a forge, for example, instead of being equal, as Wedgwood estimates it, to 17327 of Fahrenheit, is equal only to 8696. The error Guyton supposes to have arisen from Mr Wedgwood having stated the fusibility of silver too high: instead of indicating 28° on his scale as he determines it, it appears from all the experiments that have been made by others to be only 22° . That Wedgwood's degrees are actually stated too high in relation to the usual thermometrical scale, appears from some farther observations. Dr Irvine, for example, from a number of trials, found reason to believe that the heat of a common fire is equal to about 790

* Philosophical Transactions, vol. lxxiv, p. 310.

of Fahrenheit, while Wedgwood states red heat visible in day-light, which must be rather below the other, at 1077. Guyton however reduces them too low : the commencement of Wedgwood's scale, denoted by red heat, is certainly higher than 517° of Fahrenheit, the number which Guyton assigns ; for this temperature and considerably beyond it, is measurable both by mercury and oil, neither of which sustains a red heat.

With regard to the accuracy of the pyrometer, independent of this, Mr Wedgwood found from experience, that the pyrometrical pieces were liable to suffer variable contractions from circumstances in their preparation apparently minute. Natural clays, too, taken even from the same stratum, and apparently of similar qualities, differ in the contractions they suffer ; and the kind of clay which he first employed having been exhausted, he found it difficult to substitute any other, the contractions of which corresponded with the scale he had originally constructed. He was under the necessity, at length, of making an artificial compound of a clay with argillaceous earth precipitated from alum * ; but it may be doubted, whether such a composition can always be obtained uniform ; and there is some reason to doubt, if the pyrometrical pieces furnished at different periods give the same indications as those to which the scale was first adapted. The accuracy even of the method itself is doubtful ; for it is not certain if the contraction of the clay is equable, according to the temperature. If its indications, however, were uniform, it would be useful, by denoting certain points at which particular changes in bodies are produced by heat ; but from the reports given on different authorities, even this seems very questionable.

A pyrometer has been more lately invented by Guyton, in which platina, a metal not fusible even at very intense

* Philosophical Transactions, vol. lxxvi, p. 401.

heats, is employed as the measure of expansion. A rod or plate of this metal is placed horizontally in a groove framed in a mass of hardened white clay; one extremity of the rod is supported on the mass which terminates the groove; the other presses against a bended lever of platina, the longest arm of which forms an index to a graduated arc. The expansion which the rod of metal suffers from exposure to heat is indicated by the change of position in this index. The mass of clay being highly baked, does not introduce any important error from its contraction; and the alteration which it may suffer during the exposure to heat affects only the small distance between the axis of motion of the index, and the point of contact of the plate, producing scarcely any deviation. Platina not melting by any heat we have to measure, and not suffering any chemical change, is well adapted to the construction of a pyrometer*. With this instrument Guyton has given results which, as has been stated above, are very different from those of Wedgwood, and they are perhaps more accurate, at least in relation to the common thermometrical scales. He connected the whole, without any interval, from the freezing to the boiling point of water;—above this, by the medium of oil, to higher temperatures indicated by the mercurial thermometer;—and above these, to the point at which Wedgwood's scale commences, by finding the temperatures of bodies at certain stages, from the quantities of heat communicated by them to ice, in the instrument named the Calorimeter, and by indications from the expansion of air. His corrected results will be found in the Table of the Scale of Temperature, at the end of the chapter†.

Besides these, various metallic pyrometers have been

* Nicolson's Journal, vol. vi, p. 89.

† Annales de Chimie, tom. lxxiv. lxxviii. xc.

invented capable of measuring low temperatures, by the expansion being multiplied by the aid of wheels, levers, or other mechanical contrivances, or being magnified by microscopes. Such are the pyrometers of Muschenbroeck; that described by Ferguson; one invented by Ellicot, with which he measured the expansions of various metals *; one by Smeaton, applied to the same purpose †; Ramsden's, superior to the preceding ones in delicacy and accuracy ‡; Crichton's, in which advantage is taken of the difference of expansion between a rod of zinc and a rod of iron, to give a curvature to a bar composed of the united rods, proportioned to the temperature to which they are raised; by which bending, motion is given to an index that, at its other extremity, where the scale is marked, describes a considerable space ||; and one by Regnier, on a principle somewhat similar §. The accuracy of these instruments may, from the nature of their construction, be regarded as doubtful.

Since the employment of the thermometer, as a measure of temperature, more just and enlarged views have been acquired of the distribution of caloric. While the property of exciting the sensation of heat was the only one by which that power was characterised, it seemed a just conclusion, that those bodies which did not excite that sensation contained none of it. It was then the philosophical, as it is still perhaps the popular opinion, that bodies exciting the sensation of heat contain the power termed Heat or Caloric, while those which do not excite this sensation, or which excite the sensation of cold, do not, or

* Philosoph. Trans. vol. xlvii.

† Ibid. vol. xlviii.

‡ Ibid. vol. lxxv.

|| Philosoph. Magazine, vol. xv.

§ Mémoires de l'Institut National, tom. ii.

contain even a frigorific power, opposite in its nature to the other. These notions are now justly exploded. At the most intense colds, all bodies contain an immense quantity of caloric, and we are altogether unable to abstract it entirely from them. It may not be uninteresting to state the facts on which this view of the extent of the distribution of caloric is established.

That the sensations of heat or cold afford no accurate test of the caloric a body contains will be apparent from considering the manner in which they are excited. The temperature of the human body is about 96° of Fahrenheit. When any substance at a higher temperature than this is applied to our organs, it communicates caloric, and this excites the sensation of heat; when at an inferior temperature, it abstracts caloric, and this gives rise to the sensation of cold. Our sensations, however, are influenced by preceding impressions. Our body is surrounded with air, at a temperature inferior usually to the animal temperature; it is therefore always abstracting caloric from us; hence, if a body is applied to our organs, inferior to their temperature, but superior to the temperature of the surrounding atmosphere, the abstraction of caloric which it makes is inconsiderable, and, compared with the impression which the air makes upon us, it seems even positively warm. In general, then, it may be affirmed, that whatever communicates caloric to our body, produces the sensation of heat; and that the sensation of cold is excited by its abstraction; but this abstraction requires to be greater than that made by the surrounding atmosphere, to convey the sensation of positive cold. Two bodies, also, at the same temperature, will occasion different sensations, according to the rapidity with which they absorb or give out caloric. A piece of iron at 32° will feel much colder than a piece of wood at that temperature, because the former abstracts caloric more rapidly than the other; and if the iron be at a high tempera-

ture, it will feel hotter than the wood at the same temperature, as it will communicate caloric more quickly.

From these circumstances, it is evident, that the sensation excited by a body is no accurate measure of the caloric it contains; and that the sensation of cold will be excited by a substance whose temperature is inferior to the temperature of the animal body, though it may, and actually does, contain a large quantity of caloric.

That bodies at such a temperature contain caloric, is proved, by the expansion which they produce in the thermometer, if its temperature has been previously reduced; an expansion which can arise only from the communication of caloric. Or the contractions of the thermometrical fluid itself shew this in a simple manner. If the thermometer is applied to water which is freezing, the mercury will stand at 32° ; but even in the cold of this climate it falls much lower. At 32° , therefore, the mercury must have contained caloric, since it is only by the abstraction of that power that it could contract, and descend in the scale. In colder climates it descends to 40° or 50° below 0 of Fahrenheit, or 82° below the freezing point of water. At all degrees above this, it must have contained caloric; and even at that intense cold, it must have contained much caloric, since by artificial means it might be sunk lower: And if the mercury in the thermometer contained caloric at these extreme colds, all other bodies must have contained it, since it is the property of this power to diffuse itself uniformly, nor can it be accumulated in one body without being present in the contiguous matter.

Even at these intense colds, there is no reason to believe that bodies were near to being deprived of their caloric, since their particles must have been far from being in actual contact; and it is only by the repulsive power of caloric that these particles are kept asunder. This affords a more extensive view of the distribution of this

power. A solid body is to be conceived of, as consisting of particles, kept at certain distances, by the agency of caloric. When a portion of it is withdrawn, these approach nearer ; and hence the reduction of volume that takes place. But any condensation hitherto effected is very far from that in which they would be in contact, nor perhaps is such a condensation possible. The liquid and aëriform states of bodies are owing also to the presence of caloric, a liquid being merely a solid reduced to this form by its operation ; an air, a liquid brought to the elastic state by the same cause. And as there are many liquids, which require to be exposed to the most intense cold to render them solid ; and as of the airs, scarcely one has been brought to the fluid state by the most extreme artificial cold, the conclusion follows, that the lowest temperature yet produced is far from that point at which caloric would be entirely abstracted. By calculation, from principles to be afterwards stated, the point of absolute privation has been placed at at least 900° of Fahrenheit's scale below the freezing point of water.

SECT. II.—*Of the Effects of Caloric.*

THE effects produced by the operation of Caloric on matter are, Expansion, Fluidity, Vaporisation, and Ignition. Of these, Expansion is the most general, and may first be considered.

OF EXPANSION.

WHEN a body, at any temperature, is brought into contact with another at a higher temperature, a quantity of caloric passes from the hotter into the colder. The body which receives the caloric is expanded, or has its volume enlarged in every direction. When caloric is withdrawn, contraction, or diminution of volume as invariably follows. The particles approximate, and the body returns through the different degrees of expansion it had suffered when caloric had been communicated to it, until it arrive at its original volume. These changes are evident in the thermometer, in the ascent and descent of the fluid, from the operation of heat and cold; and take place nearly in proportion as caloric is abstracted.

The first important fact to be observed with regard to expansion is, that it is different, in different bodies, from the same change of temperature, being in general less as the density of the body is greater. In solids, it is so inconsiderable, as not to be perceived without accurate measurement; in liquids, it is more evident; and in airs or vapours, the least alteration of temperature is accompanied by a perceptible change of volume.

If we descend to a more minute examination of the degrees of expansion, we find, that in solids and liquids, it is

extremely various. In solids, as the expansion, from a moderate change of temperature, is inconsiderable, the difference is less obvious; but still, in those which have been the subject of experiment, it has been observed. A knowledge of the expansibilities of the different metals is of much importance in different arts, and more particularly in the construction of time-pieces; and on these, therefore, experiments have been most frequently made. The following short table, exhibiting the first accurate results,—those made by Mr Ellicot, when engaged in prosecuting his method of correcting the irregularities in the motions of time-pieces, from the influence of heat and cold on the length of the pendulum*, shews the proportions of expansion produced in different metals by the same degree of heat.

Lead.	Silver.	Brass.	Copper.	Gold.	Iron.	Steel.
149	103	95	89	73	60	56

In these results, which in a general point of view are confirmed by others, we perceive very little connection between the expansibility of solids and any of their physical or chemical properties. That it has no relation to their density, either directly or inversely, is apparent from gold being nearly at one extremity and lead at the other, though these two approach nearest in density, while copper and silver are placed between them. There is some relation between the expansion and the fusibility, those which are most fusible expanding most; and indeed, in the entire table, the expansions are stated almost precisely in the order of the fusibilities. But this does not hold invariably, as will be found from other examples, as antimony, which expands less than iron, and bismuth less than copper, though such deviations may in part arise from the errors to which the experiments are liable. The degrees of ex-

* Philosophical Transactions, vol. xlvii. p. 485.

pansion in a number of solids, founded on the authorities of Smeaton, Roy, Troughton and others, will be found in a general table at the end of the chapter.

The expansion of solids from heat is a source of error in the construction of time-pieces, the pendulum being lengthened or shortened according to the temperature, and of course its motions being varied. This error is corrected by opposing the expansion of one metal to that of another; so that in a compound pendulum, composed of two metals, properly adjusted according to their expansibilities, the expansion of the one is counteracted by that of the other, and the length remains unaltered, or the centre of oscillation of the pendulum remains at the same distance from the point of suspension. This ingenious method appears to have occurred to the artists Graham and Harrison; the application of it was executed by them in different forms*, and has since been frequently varied.

In fluids, a similar difference of expansion from heat is observed as in solids; and as their expansions are greater, these differences are more conspicuous. The expansion of water from a given change of temperature is greater than that of quicksilver from the same change, and the expansion of alkohol is greater than that of water. Taking as a standard of comparison the expansions they suffer in the rise of temperature from 50° to 100° of Fahrenheit; that of quicksilver is not more than $\frac{1}{120}$ of its volume at 50° ; that of water about $\frac{1}{113}$ of its volume at the same temperature; while that of alkohol is not less than $\frac{1}{33}$. The difference in the expansibilities of different liquids is not precisely in the same proportion at every temperature; but the general difference remains, or in these examples alkohol is at all temperatures more expanded than water, and water more than quicksilver. The expansions of the more

* Philosoph. Trans. vol. xlvii, p. 517.

common liquids, ascertained by Mr Dalton, will be found in the general table at the end of the chapter.

Since the expansions, both of different solids and of different liquids, are thus unequal from equal changes of temperature, it might be expected that different bodies existing in the aërial state would likewise expand unequally in suffering the same change of temperature. That such was the law was at one time admitted, and numerous experiments were made to determine the relative expansions of vapours and airs by Roy, Saussure, Priestley, Monge, Guyton, and others. The results of their labours were extremely discordant, though they in general agreed in finding the expansions of the different bodies of this class very different from the same augmentations of temperature.

This subject was afterwards investigated by Dalton and by Gay-Lussac, and their experiments agree in establishing the result, that all aëriiform fluids suffer the same expansion from equal augmentations of temperature.

From Gay-Lussac's experiments, it appears that 100 parts of atmospheric air are expanded by an elevation of temperature from 32° to 212° of Fahrenheit, to 137.5 parts. Hence, if the total augmentation of volume be divided by the number of degrees which produced it, or by 180° , the expansion for each degree of Fahrenheit's scale is $\frac{1}{480}$ of the original volume. The mean expansion of hydrogen gas by the same elevation of temperature was 137.52; of oxygen gas 137.48; and of nitrogen gas 137.49; differences so trifling, that they may be ascribed to the impossibility of rendering the circumstances the same in all the experiments, and indeed they are not greater than what appeared in the different experiments on atmospheric air. The experiments were extended, by a variation in the apparatus, to gases which are soluble in water; and the expansions of carbonic acid, muriatic acid, sulphurous acid, nitric oxide, and ammoniacal gases, were found the same.

The conclusion follows, therefore, that all the gases undergo the same dilatation from the same elevation of temperature. Of the vapours, that of sulphuric ether being the most easily managed, was submitted to experiment by Gay-Lussac; and by comparing its expansions above the temperature of 167° with those of atmospheric air, he found them to be alike *.

Mr Dalton's experiments established the same conclusion, that aëriform bodies undergo the same expansions from the same augmentations of temperature, 100 parts expanding in the rise of temperature from 55° to 212° to 132.1, to which, adding 0.4 for the expansion of the glass tube, we have for the expansion of the air 132.5 †. This gives as the expansion from 32° to 212° 137.3. The result of Gay-Lussac's experiments is 137.5. The expansion, therefore, for each degree, according to the former, is $\frac{1}{483}$, according to the latter $\frac{1}{480}$, an agreement as near as can be expected in experiments of this nature. The errors and discordant results in former experiments had arisen, principally from small but variable quantities of water having been admitted into the apparatus, which, passing into vapour, added to the volume of the aëriform fluid.

Bodies, therefore, existing in the aëriform state, differ remarkably from liquids and solids, in their expansions being alike from given changes of temperature.

Another important fact to be illustrated relating to expansion, is its progression with regard to temperature. It is obvious, that the progression may be regular, the expansion increasing precisely as the temperature rises, so that a double elevation of temperature shall produce a double expansion; or it may proceed either in an increasing or decreasing ratio.

With regard to liquids it has been established, that the

* Annales de Chimie, t. xliii. p. 87. Nicholson's Journal, 8vo, vol. iii, p. 207.

† Manchester Memoirs, vol. v. p. 595.

expansion does not proceed in an equal ratio, but is different at different parts of the thermometrical scale. If to water at 50° , a certain quantity of caloric be added, so as to produce a certain degree of expansion, if an equal quantity of caloric be added to the water at 60° , it will produce a different degree of expansion, and the same difference will be observed in any other temperature, and with every other fluid, though in different degrees.

The expansion in liquids is in an increasing ratio, or if a given quantity of caloric produce a certain degree of expansion at a low temperature, a similar quantity will occasion a greater expansion at a high temperature. Hence the expansibility of a liquid is least near to its freezing, and greatest near to its boiling point, and the differences between these extremes is in some of them considerable. This is very evident in water, in which the difference is more conspicuous than in any other, and at the two extremes is very great, owing to a singularity afterwards to be pointed out, in its change of volume from 40° to 32° . In cooling, one-eighth part of the interval between the boiling and the freezing points, or $22\frac{1}{2}$ degrees of Fahrenheit's scale, the condensation, as ascertained by Rumford, is as follows:—

In cooling $22\frac{1}{2}$ from	212°	or to	$189\frac{1}{2}$	18	parts.
_____	$189\frac{1}{2}$	_____	167	16.2	
_____	167	_____	$144\frac{1}{2}$	13.8	
_____	$144\frac{1}{2}$	_____	122	11.5	
_____	122	_____	$99\frac{1}{2}$	9.3	
_____	$99\frac{1}{2}$	_____	77	7.1	
_____	77	_____	$54\frac{1}{2}$	3.9	
_____	$54\frac{1}{2}$	_____	32	0.2 *	

From this it appears, excluding the irregularity at the bottom of the table, that the expansion of water in being

* Essays, vol. ii, p. 284.

heated $22\frac{1}{2}$ degrees to its boiling point, is nearly five times greater than its expansion in being heated the same number of degrees from the medium natural temperature.

In alkohol there is a similar progression in its expansibility, as the temperature rises. The following table by De Luc exhibits this by a comparison with the expansions of mercury in the mercurial thermometer, according to Reaumur's scale, assuming these, for the sake of a standard, to be regular * :—

Mercurial Therm.	Alkohol Therm.	Augmenting expansions of Alkohol, in this range of temperature.
80	80.0	6.2
75	73.8	6.0
70	67.8	5.9
65	61.9	5.7
60	56.2	5.5
55	50.7	5.4
50	47.3	5.1
45	40.2	5.1
40	35.1	4.8
35	30.3	4.7
30	25.6	4.6
25	21.0	4.5
20	16.5	4.3
15	12.2	4.3
10	7.9	4.0
5	3.9	3.9

The deviations from regularity in the expansions of quicksilver appear less than in any other liquid, as has already been observed in pointing out its fitness for the construction of the thermometer. This, however, as Mr Dalton has remarked, may in part be owing to the greater distance between its freezing and boiling points, and to a comparatively small part of this interval being submitted to experiment. And, even in this part, the increasing ex-

* Recherches, t. i, p. 252.

pansibility, as the temperature rises, is perceptible, as is evident from the following table, given by De Luc, according to Reaumur's scale* :—

Real temperature.	Corresponding points of the Mercury in the Thermometer.	Expansions of the Merc. at the respective temperatures.
80	80.8	5.3
75	74.7	5.3
70	69.4	5.2
65	64.2	5.2
60	59.0	5.2
55	53.8	5.1
50	48.7	5.1
45	43.6	5.0
40	38.6	5.0
35	33.6	4.9
30	28.7	4.9
25	23.8	4.9
20	18.9	4.8
15	14.1	4.8
10	9.3	4.7
5	4.6	4.6

Other liquids shew the same progressive expansibility as their temperature rises. Dividing that part of the thermometrical scale between the freezing and boiling of water into two equal parts, De Luc ascertained, that the expansion of the following substances in the higher division is to that in the lower in these proportions †.

	In the first division, or from 32°, to the real mean between this, and 212°, the expansion is	Ratios of the expansions in the higher division to those in the lower.
Quicksilver,	38.6	15 to 14.0
Olive and linseed oil,	37.8	15 13.4
Chamomile oil,	37.8	15 13.0
Water saturated with salt,	34.9	15 11.6
Alcohol,	33.7	15 10.9
Water,	19.2	15 4.7

* Recherches, t. i, p. 301.

† Ibid. t. i, p. 311.

De Luc found, that near to the boiling point of fluids, their expansibilities increase rapidly, and are very irregular; there are also considerable irregularities in their changes of volume at their freezing point. Hence he concluded, that their expansions would be most equable, towards the middle of the range of temperature between their freezing and boiling points; and he justly inferred from this, that the fluid best adapted, in point of accuracy, to thermometrical purposes, is that which has the greatest range of temperature between its freezing and boiling temperatures, which gives the preference to mercury. The law assumed by Mr Dalton, that the expansion in liquids is in each as the square of the temperature from the point of congelation, or of greatest density, I have already remarked is far from being established.

Since liquids expand in an increasing ratio as their temperature rises, we should be disposed to conclude, that a similar law is observed in the expansions of aëriform fluids; and, accordingly, this appeared to be established by some experiments, particularly those of Guyton and Prieur*. While atmospheric air, in being heated from 32° to 77° , expanded $\frac{1}{22.67}$, its expansion from receiving another equal increment of temperature, or in being raised from 77° to 122° , they found to be not less than $\frac{1}{3.87}$, and from 122° to 167° $\frac{1}{2.49}$. In the other airs there were similar, and in several of them greater differences. There can be little doubt, however, but that these results are erroneous, and that they arose principally from water being present in the apparatus, which passing into vapour, would give rise to the apparent greater expansion. General Roy found, in his experiments on the expansions of aërial fluids†, that the expansion is the reverse of that of liquids, or is a slowly decreasing one above the temperature of 57. And Mr

* Journal de l'Ecole Polytechnique, Cahier ii.

† Philosophical Transactions, vol. lxxvii.

Dalton found this likewise in his experiments ; the expansion for $77\frac{1}{2}$ degrees above 55° being 167 parts, while for the next $77\frac{1}{2}$ it was only 158 parts : and the expansion in every part of the scale seemed to be a gradually diminishing one in ascending *.

This apparent diminution of expansion, however, as the temperature rises, might arise from the inaccuracy of the mercurial thermometer ; the expansions of the mercury in the higher interval of temperature being greater than in the lower interval ; and the expansion in the former of 158, being therefore the result of a less real augmentation of temperature than the expansion 167 in the latter. So that making allowance for this source of error, the expansions, if the intervals of temperature were really equal, might be equable. They are truly so indeed, if we take the correction of De Luc, that the real mean temperature between 32° and 212° is according to the common scale 119.

Mr Dalton, in consequence of the hypothesis he adopted, that the expansion of quicksilver, in common with that of other liquids, is as the square of the temperature from its freezing point, and that therefore the mercurial thermometer on the common construction deviates much more from accuracy, has inferred even, not only that the expansion of aërial fluids is not a decreasing one, as appeared to be established by former experiments, but that it is progressive ; the expansion being, as he supposes, in geometrical progression to equal increments of temperature measured by the new thermometric scale †. But this conclusion rests on the assumption of this law of the expansion of quicksilver, and is therefore merely hypothetical. From more recent experiments than those before mentioned, he is convinced, that dry air of 32° will expand the same

* Manchester Memoirs, vol. v, p. 599.

† New System of Chemical Philosophy, p. 11.

quantity from that point to 117° or 118° of the common scale of temperature, as from the last term to 212. And admitting a correction for the deviation of the mercurial thermometer from accuracy, not much greater than that which De Luc assigns, the expansion will be equable with regard to temperature.

In a series of experiments, which I read before the Royal Society of Edinburgh about two years ago, and which I have not yet completed in the whole extent I had in view, I found that the contraction of a given volume of air in cooling is an increasing one as the temperature falls, or the expansion decreasing as the temperature rises. The experiment was performed by inclosing dry air in a glass ball with a long cylindrical stem placed vertical, and containing a very short column of quicksilver, the movement of which in the stem indicated, by a scale attached, the degrees of contraction at different intervals. The ball was surrounded with water, the decrements of temperature in which were observed by thermometers with great care. The following short table shews the results at intervals of temperature of 20° of Fahrenheit.

Temperature 180	Quicksilver at 54	on the scale of the tube	
_____ 160	_____ 139	contraction in this	
		interval,	85
_____ 140	_____ 231	_____	92
_____ 120	_____ 331	_____	100
_____ 100	_____ 439	_____	108
_____ 80	_____ 555	_____	116
_____ 60	_____ 679.5	_____	124.5

Here the contraction as the temperature falls increases, and this by a very regular progression, the series being 7, 8, 8, 8, 8.5. Of course these indicate the rate of decreasing expansion from these equal elevations of temperature.

These results might also be supposed to be accounted for on the principle of the thermometer not being an ac-

curate measure of temperature. But it is doubtful if the error from this is so great as has been supposed ; and even if it did operate, it must be greatest at or near the mean temperature between 212° and 32° , as from the mode of graduating the scale from these two fixed points, it is at that part that any deviation from accuracy is greatest. The contraction, however, in the above experiments, increases through the whole range of temperature from 212° downwards, and is greatest even at temperatures below 100, or below 80, a result inconsistent with the supposition of its arising from inaccuracy in the thermometer.

The only uncertainty which remains is, whether the effect may not arise from increasing expansion in the glass ball as the temperature rises, which it is evident would give rise to apparent decreasing expansion of the air, as, on the contrary, in the fall of temperature it would give the appearance of increasing contraction. Even if the expansion of solids, however, be admitted to be an increasing one with regard to temperature, it is not probable that this should be so great as to account for these results.

The more recent experiments of Petit and Dulong, it has already been remarked, give the same general result with regard to the expansion of air at higher temperatures, the expansions diminishing progressively as the temperature rises from 212° , as represented in the table, (page 222,) assuming that the thermometer indicates real increments of temperature.

The facts which have now been stated with regard to expansion may, I believe, be generalized, or the principle which connects and explains them may be pointed out. This principle is, that expansion is not simply the effect of caloric, but of caloric counteracting, by its repulsive energy, the attraction of cohesion ; and from considering it under this point of view, I would explain, in the following manner, the apparently anomalous phenomena connected with expansion.

In the first place, it has appeared, that the expansibility of solids is less than that of liquids, and the expansibility of liquids is less than that of airs. Now, in solids, the power of cohesion is greatest; the most effectual resistance, therefore, is opposed in them to the operation of caloric, and hence less expansion will be produced by its introduction. In liquids the cohesion is weaker, the expansion therefore will be greater. And in airs, as the cohesion is overcome, no resistance is opposed to the expansive force, and an enlargement of volume limited only by the pressure applied will be produced.

In different solids, the expansibility is extremely different; and, according to the view I have stated, this may be supposed to arise from the different degrees of force with which cohesion is exerted. We have no accurate measure of this force. But if we regard the different fusibilities of bodies as affording an indication of it, we find, as has already been observed, that in general the expansibility is directly as the fusibility. In liquids there likewise exist differences in the expansions they suffer; and there can be no doubt, that though in all of them the power of cohesion is weak, it may be of different degrees. If we judge of these from the volatility of bodies in this state, the disposition to volatility being less as the cohesion is stronger, we find, under the general point of view under which experiments influenced by various circumstances must be taken, that the expansibility of liquids is in a great measure as their volatility. But in substances in the aëriiform state, there is no difference in expansibility as among solids and liquids, the expansions of all being alike; and this is precisely what the theory leads us to expect. Cohesion is not exerted among *them* with different degrees of force; for in all of them it is entirely overcome. No various degrees of resistance, therefore, are opposed to the operation of caloric; and hence, under the same pressure, the same increase of temperature is followed in all aërial fluids by the same degree of expansion.

Lastly, expansion in bodies in one state proceeds in an increasing ratio with regard to temperature, while in another it proceeds equably, and to this the same principle may be successfully applied. Thus, in liquids the expansibility increases as the temperature rises, obviously from this, that by the introduction of caloric operating as an expansive power, the force of cohesion is diminished;—in proportion as the temperature rises, therefore, it becomes weaker, and opposes less resistance to the expansive energy of caloric. Hence a greater expansion must be occasioned by an equal quantity of caloric at a high than at a low temperature, because the force which opposes it is by the very increase of temperature diminished. Even to the rate at which this expansibility varies, in different liquids, the theory applies; for in examining the differences with regard to this, it appears, that the more expansible a fluid is, its expansibility by increase of temperature increases at a higher ratio. Thus mercury, which suffers the least change of volume from any given increase of temperature, is that, the expansibility of which is most equable, or increases least as its temperature is raised.

In aëriform bodies, on the contrary, we have found reason to conclude, that the expansion is not greater from a given elevation, at a high than at a low temperature, but is either equable, or even decreasing. The cause is, that in aërial fluids no cohesion exists to be weakened by augmentations of temperature; the resistance to the operation of caloric is the same, under a given pressure, at a low as at a high temperature, or at both is nothing; and the repulsive power of caloric ought therefore to act equally according to the quantity in which it is added, or the effect will be diminished only in consequence of the distance at which the particles are placed.

It follows as a consequence of this view, that in solids the expansibility ought to increase with the temperature. Their cohesion is weakened as the temperature is raised, and therefore an equal quantity of caloric ought to produce

a greater expansion at a high than at a low temperature. At the same time, the cohesion in solids compared with liquids is so great, that the same change of temperature cannot be supposed to produce the same difference in expansibility; hence the ratio of increase must be much less. Solids, too, suffer so inconsiderable an expansion from even a considerable rise of temperature, that it is not easy to ascertain the fact with accuracy. Roy, in his experiments on the expansions of metals, already quoted *, observed, that they appeared to be not equable, but progressive when tried at the temperatures of 60° , 120° and 180° : yet he seemed disposed to conclude, that when the instruments are perfect, and due allowance is made for the difficulty of keeping water (the medium by which the heat was applied) at a stationary temperature, the expansions were equable. The error, however, from this cause, might have been as well on the one side as on the other. De Luc, too, found the expansions of glass to be progressive, the expansion of a glass tube from 32° to 212° being .00083 in length, while from 32° to 122° it was only .00035: and there is nothing peculiar to glass, to lead to the belief, that this increasing expansion is not a property of it in common with all solids. His experiments, however, from the mode of conducting them, were liable to some doubt. Lavoisier and La Place inferred from some trials, that the expansions of metals from the temperature of freezing to that of boiling water correspond with the indications of the mercurial thermometer. Petit and Dulong have more lately made this the subject of experiment. They have found, as has been already stated, (page 223,) that the expansion of metals above 212° is progressive, or exceeds that of the mercurial thermometer; and they farther found reason to infer that the expansibility of glass is also progressive, and this even in a higher ratio than that of metals †.

* Philosophical Transactions, vol. lxxv.

† Annales de Chimie et Physique, t. ii, p. 254.

There remain to be noticed some exceptions to the law that bodies are expanded by caloric.

The most general is that enlargement of volume which many substances suffer in passing from the liquid to the solid form. When a liquid is cooled, it contracts with more or less regularity until it reach the point at which it becomes solid. But at the moment that it congeals, instead of remaining of the same volume, or of contracting, it in different instances expands with considerable force. This is remarkably the case with water; its expansion in freezing is capable of overcoming a great mechanical resistance. Boyle found, that by the freezing of a small portion of it, a weight of 72 lbs. was raised. The Florentine Academicians made some experiments, in which a brass globe, the cavity of which was an inch in diameter, was burst by this expansive power; and calculating from the tenacity of brass, and the thickness of the sides of the globe, this must have required a force exceeding 27,720 pounds. Major Williams obtained similar results, an iron plug $2\frac{5}{6}$ lb. weight, being projected from a bomb-shell to the distance, in one experiment, of 415 feet, with a velocity of more than 20 feet in a second, and in another experiment the shell being burst *. The amount of the expansion was calculated to be equal to $\frac{1}{17}$.

From this expansion of water in freezing, the specific gravity of ice is always inferior to that of water, as is evident from its floating on the surface of water.

This expansive force has been ascribed to the extrication of a portion of air which water holds in solution, and which freezing disengages. Though this may have some share in the effect, it is far from being the sole cause; as the expansion takes place when the water has been freed as much as possible from this air, by the air-pump. An experiment of this kind was made by Boyle †.

* Transactions of the Royal Society of Edin. vol. ii, p. 23.

† Boyle's Works, vol. ii, p. 516.

Mairan explained it on the supposition of a polarity in the particles of the water, or a tendency to unite by certain sides in preference to others; to arrange themselves in a certain manner, and run into right lines at determinate angles. The explanation appears to be just. When the freezing of water is examined by the microscope, this peculiarity of arrangement is observed, the lines shooting out from each other at an angle either of 60° or of 120° . A similar arrangement is conspicuous in a flake of snow. The freezing of water, therefore, is a species of crystallization, and, from the arrangement it produces, vacuities are formed in the solid mass, and its volume, compared with the fluid, is enlarged.

The same phenomenon is perceived in some other substances. Iron, in becoming solid, expands, and hence the delicacy of the impression it receives from a mould. So do bismuth and antimony, and perhaps some other metals: others, as quicksilver, conform to the more general law, and suffer contraction. Sulphur, according to Dr Irvine's observations, expands in congealing. In the crystallization of saline solutions by exposure to cold, expansion often takes place; not always, however, for both nitric and sulphuric acid contract in congealing, though their congelation is a species of crystallization.

But a phenomenon still more singular is exhibited by water. It expands, not only in the moment that it passes to the solid form, but before it reaches its freezing point. This expansion appears when the temperature of the water is reduced to 40 of Fahrenheit, and continues in an increasing ratio until it freeze. This seems first to have been observed towards the close of the 17th century, by the Members of the Academy del Cimento. It was some years afterwards announced by Dr. Croune to the Royal Society, and even then its reality was disputed by Hooke, who ascribed the appearance of it to the contraction of the vessel. So little attention was afterwards paid to the ob-

servation, that it seems to have been forgotten, until again mentioned by Mairan. De Luc first investigated it with precision *. He fixed the point at which the expansion commences, at 41° of Fahrenheit; and he supposed the expansion from that point, either towards a higher or lower temperature, to be the same; so that the density of water at 50° and at 23° is alike.

It was observed by Blagden, that if, by avoiding agitation, the freezing of water at 32° be prevented, and it is cooled to 21° or 22° , the expansion continues to proceed, and in an increasing ratio; or, if its freezing point be reduced, by dissolving certain salts in it, the expansion begins at about the same distance from the point at which such a solution does freeze, as that which pure water observes †. At a subsequent period, he endeavoured to determine the difference of density in water at these temperatures by weighing, endeavouring at the same time, from the known expansibility of glass, to make due allowance for the difference in the capacity of the containing vessel from the difference of temperature; he inferred the specific gravity of water at 35° to be to that at 40° , as 1.00087 to 1.00091, that at 60° being 1.00000 ‡. But from the very different expansibilities of glass, and the difficulty of the experiment, much confidence cannot be placed in this calculation. Le Fevre Gineau found also by weighing that the greatest density of water is at 39.2 of Fahrenheit.

Mr Dalton likewise made this the subject of experiment. He fixed the maximum of density at $42\frac{1}{2}^{\circ}$ of Fahrenheit. From 41° to 44° the expansion is barely perceptible; from either of them it proceeds in an increasing ratio, and in

* Recherches sur les Modifications de l'Atmosphere, tom. i, p. 225, &c.

† Philosophical Transactions, vol. lxxviii.

‡ Ibid. vol. lxxx, p. 333.

the reduction of temperature from 41° to 32° , the expansion amounts to about $\frac{1}{100}$ part of the whole expansion from $42\frac{1}{2}^{\circ}$ to 212° . He confirmed the observation of De Luc, that the expansion for any number of degrees, either above or below the point at which it commences, is the same; so that, taking this point at 42.5 , the density of water must be the same at 32° and at 53° ; or, if it be at 40° , at 32° and 48° . He confirmed also the observation of Blagden, that the expansion continues below 32° when the water is cooled beneath that without freezing, and this at a very high ratio. He succeeded in cooling it so far, that the water, from expansion, had risen as high as the point to which it would have been raised had it been heated to 75° . Its real temperature must then have been 10° . On freezing, it rose suddenly to 128° on the scale*.

Mr Dalton, from subsequent investigations, considered this anomaly exhibited by water as apparent, not real, explaining it in the same manner as Hooke did, from the contraction of the vessel in which the experiment is made. The usual mode of making the experiment is, to put a quantity of water into a ball with a cylindrical stem, of narrow bore, similar to a thermometer, and to cool it, the expansion of the water, in cooling, being measured by its ascent in the tube. It is evident, that the glass ball being cooled, must contract, and must contribute in part at least to the rise of the fluid. On the supposition, however, that the whole effect depends on this, it may be inquired why is it not exhibited by other liquids, and why should it appear only at the part of the thermometrical scale at which it does? Both these objections may be obviated. The reason why the apparent expansion is exhibited only by water may be said to be, that it is the liquid in which the changes of volume at that temperature are least considerable; they are therefore inferior even to the contractions of glass; while, in other liquids, the contractions being more considerable,

* Manchester Memoirs, vol. v, p. 374.

they are not exceeded, or even equalled by the contraction of the instrument, and, though no doubt lessened by it, are still apparent. The reason why the apparent expansion of water takes place only as it approaches its freezing point, is, that its expansibility is in an increasing ratio with regard to temperature. The farther it is cooled the less considerable are its contractions from decrements of temperature; and continuing to diminish, they are at length inferior to the contractions of the glass, and from this point the apparent expansion must begin.

So far the opinion is not improbable; and the experiments by which Mr Dalton endeavoured to establish it appeared not inconclusive. If the explanation, which refers the rise of the fluid in the tube to the contraction of the vessel, be just, that rise must be different in extent, and in the point at which it commences in vessels of different kinds of materials; for the expansion of any substance being peculiar to itself, their contractions from cold must be different, and their effect, of course, in pressing on a contained fluid must be unequal. On this idea he repeated the experiments in vessels of earthen-ware, and of different metallic substances, and found the point of maximum density to be different in each. The following table shews the differences:

				Water lowest.	Water the same height.
Brown earthen-ware,	-			at 38°	at 32° and 44°
White earthen-ware,	-			40	32 and 48 +
Stone ware,	-	-		40	32 and 48 +
Flint glass,	-	-		42	32 and 52½
Iron, thin plate,	-	-		42 +	32 and 53
Copper,	-	-		45 +	32 and 59
Brass,	-	-		45½	32 and 60
Pewter,	-	-		46	32 and 60½
Zinc,	-	-	-	48	32 and 64 +
Lead,	-	-	-	49	32 and 67*

* New System of Chemical Philosophy, p. 31.

The conclusion, however, which Mr Dalton drew from these experiments, does not follow. The containing vessel must no doubt influence the result; and from this the point at which the expansion commences must be somewhat lower than it appears; and will appear highest in a ball made of a substance which contracts most from a reduction of temperature, and lowest in one which suffers little contraction. The influence of this is apparent in the preceding experiments, lead, for example, being the metal which suffers the greatest contraction, as appears from the table of Ellicot, in a ball of lead, the point of greatest density is raised highest in the thermometrical scale, or appears at 49° , while glass and earthen-ware are inferior to metals in expansibility. Still the conclusion cannot be drawn, that the contraction of the vessel is the sole cause of the ascent of the fluid. On the contrary, as the expansibility of earthen-ware is so inconsiderable, it may be inferred, that in the reduction of its temperature, from 40° to 32° , the contraction is so small, as to contribute little to the apparent expansion of the water; and that, therefore, the result of the experiment with it proves nothing more, than that the point of greatest density is lower than had been supposed; and even with regard to this, there may be some fallacy from the porosity of the earthen-ware. In making due allowance for the expansibility of brass, iron, copper and lead, compared with glass, the point of greatest density in water will appear in fact, from these experiments, to be about 38.5 .

The reality of this anomaly in water has since been established fully by Dr Hope, by experiments conducted in a manner altogether different from the preceding, and free from the objections to which they are liable; the effect being inferred from the change of place in a column of water, cooling from 40° to 32° , or heating from 32° to 40° , and being therefore independent of any contraction or expansion of the vessel.

A cylindrical glass jar, $8\frac{1}{2}$ inches deep, and $4\frac{1}{2}$ inches in diameter, was filled with water at 32° , a thermometer being suspended in it, nearly in the axis, so as to have its bulb distant half an inch from the bottom; and another being placed at the same distance from the surface of the fluid. Being exposed to the air of a room, at the temperature of 60° , the temperature of the water was gradually raised; and did it expand from this rise, it is obvious that it must rise towards the surface, and that while any inequality of temperature existed in the mass, the thermometer there must indicate a higher temperature than the thermometer near to the bottom; while if it contract from the addition of caloric, the reverse must happen. The result of the experiment was, that in the progression of temperature up to 38° , the thermometer at the bottom was always one degree at least higher than that at the surface, a sufficient proof that the water, as its temperature rose from 32° , had become more dense.

In the cooling of water to 32° , a similar result was obtained; the thermometer at the bottom remaining higher than that at the surface. And this experiment was conducted, so as to shew clearly the accuracy of the method; for when the water was taken of the temperature of 53° , in cooling to 40° , the colder water was found at the bottom; the difference between its temperature, and the temperature of that at the surface, amounting even to 7 or 8 degrees. When the fluid at the bottom attains 40° , it remains at that until the whole reaches that point; and then the progress of the cooling begins to be reversed, or the colder fluid now is found at the surface, while that at the bottom is four degrees warmer.

These experiments were varied, and rendered more striking by communicating or abstracting caloric, not to or from the entire mass of fluid, but at the surface, the middle, or the bottom of the vessel. Above 40° , the warm-

er part of the fluid always is at the top of the vessel, while the colder is found at the bottom. Below 40° this arrangement is reversed, the warmer part is of greater density, and descends; the colder, being more expanded, is elevated to the surface, where it remains. In communicating heat or cold to the middle of the jar, the determination of these currents is well displayed. The whole experiments establish the conclusion, that the point of greatest density in water is not at its freezing point, but a considerable number of degrees above it; and that as it approaches to that point it suffers expansion*.

Mr Dalton has since admitted, that the point at which water is of the greatest density is not at 32° , but, as he supposes, about 36° ; and he has employed a good deal of reasoning to shew, that from Dr Hope's experiments it cannot be inferred to be higher than this †. Whatever may be the exact point, the result of importance is, that this anomaly with regard to water exists; and this is fully established; and it must be difficult to ascertain it with perfect precision, for the expansion being an increasing one, wherever it commences, it must in the first stage be inconsiderable. It is probably near 38° . A confirmation of this is found in nature on a large scale, in the uniformity of the water of deep lakes, at about 40° or 41° . Pictet pointed this out with regard to a number of lakes in Switzerland, and it is evidently owing to this being the point of maximum density of water, so that if the water were either heated or cooled beyond this at the surface it would not descend ‡.

Considering the fact as established, it is a subject of inquiry if any cause can be assigned for this anomaly. The explanation stated by Sir Charles Blagden has been ge-

* Transactions of the Royal Society of Edinburgh, vol. v.

† Nicolson's Journal, vol. xiii, p. 377; and vol. xiv, p. 128.

‡ Rumford's Essays, vol. ii, p. 297.

nerally received;—that that peculiar exertion of the attraction of cohesion, which gives rise to the arrangement of the particles, so as to unite them in symmetrical forms, may commence some degrees before the point at which it becomes sufficiently efficacious over the repulsive power of caloric to produce solidity; and this arrangement may produce enlargement of volume, which shall exceed even the contractions that would result from the abstraction of caloric.

It might be supposed, that were this explanation just, the water should suffer some diminution of its fluidity, which from an experiment Dr Hope made with the gravimeter, he infers, does not happen. The experiment, however, is liable to some fallacy, from the operation of temperature on the instrument, the exact amount of which it is not easy to estimate. Since cohesion exists in fluids, it seems scarcely to be doubted, but that its force will be diminished by increase of temperature; and the conjecture that it is, appears to be established by an observation made by Mr Leslie, that from this cause water drops from a small tube with six times more velocity when it is near its boiling point than when it is on the verge of congelation*. There is here also, however, a source of fallacy, in the difference in the diameter of the aperture, produced from the expansion of the substance of the tube; but there is reason to believe, from the known expansibility of glass, that this is not sufficient to account for the difference; and the general deduction from theory may be regarded as sufficiently probable, that the cohesion of fluids must vary with temperature, though the extent of the variations cannot well be determined.

There is reason to believe, that in other fluids, which expand in the act of congealing, this expansion takes place through a certain range of temperature above the

* Philosophical Magazine, vol. xiv. p. 204.

point of congelation. Mr Mushet remarked, that if on pieces of iron, melted iron be poured, they float, and expose a considerable portion of their bulk above the surface of the liquid iron, a proof of the greater density of iron in its fluid than in its solid state. But this buoyancy diminishes; and as the pieces of metal approach more and more to the state of fusion, they gradually sink, till they disappear entirely under the surface*; from which it may be inferred, that, in proportion as the temperature of the melted iron is reduced, its density is diminished.

There is one other exception to the law of expansion from caloric,—that observed in the different clays and the pure earth, alumina, which predominates in their composition. These contract, instead of expanding by increase of temperature. It is on this property of clay, that Mr Wedgwood constructed his pyrometer; and he ascertained the principal facts with regard to it. The contraction is irregular at temperatures below ignition, and seems to proceed principally from dissipation of moisture, and expulsion of aërial matter. At the approach to ignition, a slight enlargement of volume is observed, and is accompanied with an extrication of air; but at a full red heat, contraction again takes place, and from this point proceeds, as the temperature is raised, until the heat is sufficiently intense to produce vitrification: when this takes place, which happens at different degrees of heat in different clays, the property is lost. Through this stage the clay remains porous, and is bibulous, but at the same time acquires great hardness. The whole contraction it suffers is equal to one-fourth of its volume. When it begins to vitrify, it expands, and by urging the heat, it is converted into a slag, and is contracted into less volume than the clay occupied in any of its preceding states.

It is difficult to assign the cause of this anomalous pro-

* Philosophical Magazine, vol. xviii, p. 8.

perty in clay. As the contraction is permanent, remaining when the clay has become cold, it might be supposed to depend on some change of composition. It has been supposed to be owing to the expulsion of volatile matter, particularly of water, which clays retain with force, and which may be gradually expelled, as the heat rises in intensity. But this supposition seems to be refuted, by the fact ascertained by Wedgwood, that his pyrometrical pieces, at very high temperatures, sustained no diminution of weight, though they continued to contract. At a low red heat, a disengagement of common air with carbonic acid takes place; from that to a strong red heat there is a loss of weight, amounting to about two parts in the 100. But past this there is no further loss. This has been ascertained also by Saussure. The pyrometrical pieces he employed lost $2\frac{1}{2}$ grains by heating to the 29th degree of the scale; but beyond that, to the 170th, they lost no weight, though diminished one-fourth in volume*.

It may probably be ascribed to the exertion of the attraction of cohesion being favoured by the heat, so as to give rise to a closer aggregation. What renders this probable is, that the clay acquires hardness, according to the heat to which it has been exposed; and that, at length, it is with difficulty acted on by substances, in which, in its natural state, it is easily soluble. Sir James Hall, in his experiments on heat modified by compression, observed, that chalk suffers changes somewhat analogous to these; a solid piece which had been previously measured in the gage of Wedgwood's pyrometer, suffering, when heated under compression, a contraction three times greater than that of the pyrometer pieces in the same temperature; it lost nearly its power of imbibing water, and acquired additional specific gravity, proving the approach of the particles during their consolidation†.

* Philosophical Magazine, vol. x, p. 155.

† Edin. Philosoph. Transact. vol. vi.

With the exceptions which have now been stated, all bodies which have not their composition or texture permanently changed by caloric, suffer expansion from its introduction, and contract again when it is withdrawn.

OF FLUIDITY.

THE second general effect produced on bodies by the action of caloric, is Fluidity, or their conversion to the liquid state.

It has appeared that, when caloric is introduced into a body, the volume is augmented, or the particles are separated to greater distances from each other. This continues to go on in proportion to the increase of temperature, until the particles are separated to such distances as to be easily moveable in every direction. This constitutes the fluid form. By a reduction of temperature the particles approach; when within certain distances they unite, and the fluid is brought back to the solid state.

These changes of form depend on the relative action of caloric, and of the force of cohesion. By the attraction which subsists between the particles of bodies, they are made to approach, and are united, so as to form solid masses. Were this power only exerted, all bodies would appear under this form, their particles would be in actual contact, and every mass would be equally dense. But its force is counteracted by the repulsive agency of caloric, by which the particles are separated to distances at which the attraction ceases to operate with much force, or by changes connected with their positions, is so far modified in its mode of exertion as to admit of the transition of the body into the fluid form.

Yet fluidity is not to be regarded, as has often been af-

firmed, as consisting merely in the weak cohesion existing among the particles, in consequence of the distance at which they are placed by the action of caloric; it rather depends on a new arrangement accompanying this, or produced by it. Cohesion exists in the fluid, and it is not easy to determine to what extent; and that a change in the position of the particles of the body, so that they assume one which is determinate, takes place, is proved by the facts which have been stated with regard to the contraction some substances experience in becoming liquid,—facts inconsistent with the hypothesis, that fluidity depends on a weaker cohesion from the particles being placed at greater distances. The view given of this subject by Professor Robison appears to be just *. He remarked, that to explain the mobility of a fluid, or the facility with which its parts are separated, it is necessary to suppose only that the action of its particles, whatever it may be, is equal in every direction, at the same distance; as if there exist this equality, it can require no force to move an adjacent particle from one situation to another; nor any force to keep the particle in its new situation with regard to the rest of the fluid. And still the attraction exerted between the particles, provided it be equal, may be strong. On the other hand, in a solid, the particles must attract more strongly in one direction than in another; hence a particular situation of each particle must be assumed, and a force, more or less great, will be requisite to change its position. It follows, therefore, from this view, and from the preceding facts, that fluidity arises not merely from the weakness of cohesion between the particles, but also from the change in the mode in which they attract each other. But this, at the same time, arises from the expansive energy of caloric, which, in separating the particles to certain distances, gives rise to this change in their mutual action; whence they assume different posi-

* Black's Lectures, vol. i, p. 517.

tions, and attract with a different but equal force. It is probable that this depends on the modification introduced by the figure of the particles of bodies. Within a certain distance this must operate in the strength of the attraction they exert; and they will be retained in a certain position rather than in others. But when, by the repulsive agency of caloric, they are placed at greater distances, this will cease to operate, any effect from figure must be insensible, and the particles will attract equally in all directions,—the circumstance which constitutes the liquid form.

Fluidity thus arising from the operation of caloric cannot, it is obvious, be regarded as essential to any species of matter. Solidity is the natural state of every body; and there can be no doubt but that every fluid is capable of being rendered solid by the necessary reduction of temperature. Every known liquid nearly has been reduced to the solid state; and the difference in the degrees at which different bodies suffer this change of form, depends entirely on the relative force of cohesion. Where that force is weak, the fusion may take place at a low temperature; and the body will be met with in the liquid form, unless in extreme colds; but such bodies cannot be considered as more naturally fluid than others.

There is also no solid but what may be rendered fluid by the due increase of temperature, though some require a great rise compared with others. Tin, the most fusible of the metals, melts at 442° of Fahrenheit, while platina cannot be melted in the strongest heat a furnace can raise. The substances most difficult of fusion are the pure earths; but the greater number of them have been fused by the intense heats which the researches of modern chemistry have enabled us to excite.

In common language, those bodies which are liquid at the medium temperature of the globe are said to be frozen or congealed when they are brought to the solid state; and those which are solid at that temperature, when they

are rendered liquid by an addition of caloric, are said to be melted or fused. The changes, however, are the same; and water is as much to be considered as melted ice, as lead or iron when it is in the fluid state is the melted metal. In a general table of the scale of temperature, at the end of the chapter, will be found the temperatures at which a number of bodies suffer this change of form.

To guard against mistake, it may be observed, that there are many substances which we cannot melt; such are the greater number of the animal and vegetable products. A piece of wood, for instance, cannot be brought into a liquid state by any application of heat. But the reason of this is, that such bodies suffer decomposition at a temperature lower than that which would be necessary to fuse them; the balance of attraction between their elements being broken, so that they pass into new combinations. It is thus that a piece of wood, instead of being fused by heat, is converted into water, an acid liquor, and several other new products. But such cases furnish no just exceptions to the universality of this effect of caloric.

Of the fusion of substances when their decomposition is prevented, we have a striking example in the experiments of Sir James Hall. By the application of pressure, so as to prevent the decomposition arising from the separation, by heat, of ærial or volatile ingredients, he succeeded in fusing marble, limestone, or chalk, and likewise coal, which, by exposure to heat, without this management, could not be melted. These experiments, too, so far establish a general principle with regard to fluidity, that when an elastic body, or one which in its insulated state is ærial, is combined with a solid, if its escape is prevented by sufficient pressure, it renders the solid fusible at a lower temperature. Lime, in its pure state, is not melted by the most intense heat which a furnace can raise, but, when combined with carbonic acid, it is melted at a temperature, according to Sir James Hall's experiments, not

greater than 25° of Wedgwood. The aërial ingredient seems to share its facility of being expanded by caloric with the solid, and thus to increase the fusibility of the latter.

There is a remarkable difference between expansion and fluidity, in the manner in which they are effected. Expansion is produced gradually, there being as many degrees of it as there are degrees of temperature, while fluidity is in general sudden, and takes place at a precise temperature. If a body be within even one degree of its melting point, it preserves its solid form. There are some substances, however, which become soft before they pass into the state of liquids, as those of an unctuous nature; and the same thing is observable in some of the metals. In the solder of the pewterers, for example, the interval between the commencement of congelation and the solidification of the mass is not less than 40 degrees. The cohesion of a fluid is lessened, or its tenuity and mobility are augmented, by increase of temperature. In a tube .0674 inch in diameter, 33 long, a reservoir was half emptied in $35' 34''$ at 100° of Fahrenheit; in $60' 58''$ at 55° ; and in $76' 19''$ at 41° *.

In the reduction of liquids to the state of solids, there are some circumstances which have an influence in producing the change, independent of the mere abstraction of caloric. When ice is raised to 32° of Fahrenheit, it invariably melts, nor is it possible to raise its temperature one degree higher, as any addition of caloric only serves to melt it more rapidly. But water may be cooled below 32° , without being converted into ice; it may be cooled without difficulty to 27° , 25° , or 23° ; Blagden succeeded in cooling it to 21° of Fahrenheit, De Luc cooled it 6 or 7 degrees lower, and Mr Dalton has brought it so low as 5° of Fahrenheit without freezing.

* Young's Natural Philosophy, ii. 396.

Other circumstances, therefore, influence this change of form besides temperature. The most general is agitation. In cooling water below 32° , to prevent freezing it must be done slowly, and with perfect rest. It otherwise freezes at 32° ; or if we have succeeded in cooling it below that, agitation instantly causes it to freeze, and the temperature rises to the freezing point. This was observed by Mairan. Blagden remarked, that the kind of agitation which favours freezing is rather that which occasions a vibration among the particles than that which moves the mass: hence striking the vessel containing the cooled water against a hard body produces instant congelation, when agitating it in the hand will not have the same effect.

Water which has been deprived of air by boiling, or other means, it has been supposed, can bear reduction of temperature without freezing better than water in which air is contained. The reverse of this, however, was established by Dr Black. He exposed equal quantities of water unboiled, and water which had been boiled for four hours, to a cold atmosphere, and found that ice was always formed first in the boiled water, and that frequently when ice was on its surface the other remained liquid, though the moment it was agitated spiculæ of ice formed, proving that it had been cooled below 32° . Hence, he remarks, the reason of the practice in India, of boiling water intended to be employed to obtain ice. He supposed this peculiarity in boiled water to arise from the circumstance that its air having been expelled, it again absorbs it, when exposed to the atmosphere; and this may occasion a slight motion among the particles at its surface, by which the congelation may be accelerated *. The effect is analogous to the crystallization of a saturated saline solution from the admission of the air.

* Philosophical Transactions, vol. lxxv, p. 8.

The intermixture of any particles that impair the transparency of the fluid have a similar effect; so that it cannot be cooled two degrees below 32° without freezing.

The circumstance, however, which, with most certainty, determines the congelation of water, is the introduction of the smallest particle of ice or snow; crystals instantly shoot from the spot the ice touches, until the whole surface is frozen. This is well illustrated in an experiment of Sir Charles Blagden's. In a calm day, when the temperature was about 20° , two vessels with distilled water were exposed to the atmosphere; one slightly covered with paper, the other open; the former bore to be cooled many degrees below the freezing point, while a crust of ice formed on the surface of the other, before the thermometer immersed in the middle of it came to the freezing point. The phenomenon had been before observed: he justly ascribes it to frozen particles floating in the atmosphere, which when they touch the cooled surface of the water cause it to freeze. Oil poured on the surface of water prevents it from freezing so readily, evidently by preventing the influence of this cause.

The phenomena now stated have usually been explained on the principle, that the congelation of a fluid, such as water, is a species of crystallization, in which the particles are peculiarly arranged. The existence of such a polarity, or disposition to unite by certain surfaces in preference to others, seems to be proved by the lines of ice shooting out at certain angles, and by the transition of form being accompanied with an enlargement of volume; and it affords a satisfactory solution of the operation of the different circumstances which influence the transition. When the fluid is cooled, its particles approximate; but the surfaces presented to each other may not be those disposed to unite. *Agitation*, by the various motions it impresses on them, may occasion some to pass into a more advantageous position, or to approach nearer to each other; and these ef-

fects are more likely to happen from an internal agitation than from a general motion of the whole mass. Extraneous substances, besides serving as points from which attraction may be exerted, may, by various chances attending their floating in the water, throw the particles into favourable situations. Lastly, the influence of a particle of the solid is evidently to be ascribed to the attraction it exerts to the contiguous particle of the liquid, an effect which, when it is sufficiently energetic to cause the crystallization to commence, will quickly be extended through the whole mass *.

Other fluids besides water exhibit the same phenomenon. Mr Macnab found, that nitrous acid might be cooled from 30° to 40° below its usual freezing point; and a similar observation has been made on sulphuric acid, and on mercury. A decisive proof of it is, that they can be cooled considerably without congealing; but the moment their congelation commences, their temperature rises a number of degrees. Blagden found, that the same thing happens in many saline solutions. The dissolving a salt in water generally depresses its freezing point; but the property of bearing reduction of temperature a number of degrees below the point of congelation still remains. If water, for example, hold sea-salt dissolved, its freezing point is reduced to 16° , but it can with care be cooled to 9° , without freezing; and a solution of nitre, the freezing point of which is 27° , can be cooled to 16° . These facts admit of a similar explanation.

During liquefaction, a quantity of caloric is absorbed by the fluid, which does not augment its temperature; and when it returns to the solid state, this caloric is again rendered sensible. This is a chemical phenomenon of the first importance, but it will with more advantage form the subject of a separate section.

* Philosoph. Traus. vol. lxxviii, p. 141.

OF VAPORIZATION.

WHEN a body has been rendered fluid by caloric, by a farther rise of temperature it is expanded in the same manner as when solid. This expansion continuing to increase as the temperature is raised, the particles are at length separated to such distances that a change of form again takes place; the attraction of cohesion is overcome, a repulsive or elastic power is acquired, and the body becomes rare and invisible, or passes into the æriform state. This is the third general effect of caloric. It is properly termed Vaporisation.

Examples of this change are sufficiently familiar. When water is heated to 212° of Fahrenheit it begins to boil. This ebullition is the conversion of the water into vapour, and the rise of the vapour through the fluid produces the appearance of boiling. In a certain time the whole will be dissipated under this form. Other fluids, as alkohol, or ether, or a number of solids, as sulphur, camphor, &c. may be made to suffer the same change.

This process of vaporisation has been distinguished from another, in which a body likewise escapes under an invisible elastic form, that of Evaporation. When water is exposed to atmospheric air, it is dissipated and at length entirely disappears. A number of other bodies suffer the same change. This is termed Spontaneous Evaporation. It has been regarded as the solution of a body, solid or liquid, in an aerial fluid. Vaporisation, again, is the rapid conversion of a body into an elastic vapour, by the operation of caloric alone.

This invisible elastic form, into which many substances are brought by the agency of this power, is termed the gaseous or æriform state; and when existing in it, they are named Vapours, Airs, or Gases. The two latter terms,

Air and Gas, used in a generic sense, are synonymous; they are applied to denote those bodies which exist in this invisible elastic state, and which by reduction of temperature are not rendered liquid or solid. Vapours, again, are condensable; but while they exist in the state of vapours, they possess the same mechanical properties as airs.

The distinguishing property of bodies existing in the æriform state, is elasticity, or the capability of being reduced into a smaller volume by pressure, and of expanding when that pressure is removed. All the airs and vapours are possessed of this property, and it is nearly peculiar to them; for though water and some other fluids seem to be compressible and even elastic, this is in so inconsiderable a degree, as to be scarcely perceptible; while elasticity is possessed so remarkably by all the gases, that it is their most distinguishing property.

The compressibility of any of these bodies is obvious, even on a very moderate pressure. The weight of a few inches of mercury is sufficient to reduce the volume of atmospheric air, or any other gas, very perceptibly. By a strong pressure, atmospheric air has been reduced to the 128th part of its volume. By mere compression, the vapours can be reduced to the fluid state.

Their elasticity is exerted with great force. If any fluid, such as water, alcohol, or mercury, be heated in a vessel from which the vapour cannot escape, the vessel will be burst, though made of metal, and of considerable thickness. The elasticity of watery vapour is applied with great force, and to the most important practical purposes, in the steam-engine, a machine in which it is the sole spring of motion, productive of immense power.

The elasticity of the gases is greatly augmented by increase of temperature. It has been already stated, that the volume of atmospheric air is increased by this cause in the proportion of $\frac{1}{480}$ th part for each degree of Fahrenheit's scale; and the elasticity of the vapour of water or

of alkohol is nearly doubled by every 30 degrees of Fahrenheit above 212°.

Rarity is another property, distinguishing bodies in this form. The particles are separated to such distances that the portion of gravitating matter in a given volume is comparatively small. So few rays of light too are reflected, that no impression is made on the organ of vision; hence bodies in this state are invisible, except in the example of two or three elastic fluids, which are distinguished by peculiar colour; or where, as in the atmosphere, from the largeness of the mass some tint of colour is displayed. The vapours in condensing become opaque; but this is owing to a part having assumed the fluid form, and being diffused through the remaining vapour.

It is scarcely necessary to add, that gravity is a property possessed by all the vapours and gases, since they consist of solid matter, brought into this form by caloric; though from their great rarity they are much inferior in specific gravity to solids or liquids. The discovery of the weight of the elastic fluid which forms the atmosphere, as it was one of the first fruits of the researches of modern experimental philosophy, was also the first step in the investigation of the properties of aërial fluids.

The point at which bodies pass into the aëriform state is very various. Some assume it at so low a temperature, that the greatest cold that has been produced is insufficient to reduce them to the fluid form. Others, as ether, alkohol, water, or quicksilver, are convertible into vapour by a moderate heat; ether, for example, at 104°, alkohol at 176°, water at 212°, quicksilver at 672°. These are therefore easily reduced to the state of fluidity; while there is a third class of bodies, such as the metals and earths, which are not converted into vapour but by the most intense heat; there are even some of them which have not suffered this change. These are termed Fixed, in contradistinction to those which are volatile or easily

convertible into vapour; but the term is merely relative, since there can be no doubt but that even these bodies are volatile, though at a higher temperature than we can easily produce.

By combining a fluid with a solid having an affinity to it, the transition into vapour is prevented or retarded; by dissolving certain saline substances, for example, in water, its boiling point is raised a number of degrees, the affinity of the salt to the water counteracting its volatilization, and hence the effect is, generally speaking, in proportion to the force of the affinity, and the quantity dissolved. Achard stated that some salts dissolved in water have the opposite effect of lowering its boiling point, but according to Gay-Lussac this is not the case. If a more volatile body, however, be combined with another, and at the same time exert to it a strong affinity, the volatility of the latter is increased.

The difference in the degree of temperature, at which bodies assume the aërial form, has given rise to the distinction established in chemical language between vapours and airs or gases. The former consist of bodies which, at a certain temperature, assume the gaseous form, that is, acquire elasticity, are rarified so far as to become invisible, and are so light as to ascend in the atmosphere; and which, while in that state, are compressed by pressure, and expand when that pressure is removed, providing their temperature be kept up; but as soon as their temperature is reduced to a point lower than that at which they were converted into a state of vapour, they return to the fluid form. The latter form another class likewise invisible, compressible and elastic, which differ from the former, in being not reducible by cold or pressure to the liquid or solid state. These are named *Airs or Gases*, and are distinguished by the property of permanent elasticity. Atmospheric air is one of these, and there are a number of others, distinguished by peculiar chemical properties.

The same opinion has been entertained of airs, that was formed respecting those bodies which were always found liquid. Their aëriform state has been considered as natural or essential to them. But modern chemistry demonstrates, that they owe their form to the presence of caloric, and that could this be sufficiently abstracted, they would, like the vapours, be reduced, first to the liquid, and then to the solid state.

This important proposition, though even in the present day sometimes objected to as an hypothesis, is sufficiently established. It is nearly proved *a priori* from the known agency of caloric, which converts solids into liquids, and liquids into vapours. These vapours possess all the mechanical properties of airs; and it is demonstrable, that if the bodies existing in the state of vapour had assumed that state at a lower temperature, they would possess the only distinguishing property of airs, permanent elasticity. If water, instead of requiring a temperature of 212° to convert it into vapour, suffered that change at 20° or 30° , it is evident that at 50° , 60° , or any superior temperature, it would be an air, or, in other words, permanently elastic; and if we suppose its point of vaporization to be still lower, to be 100° or 200° below 0 of Fahrenheit, it would be permanently elastic at any reduction of temperature we could command, and of course perfectly analogous, in its mechanical properties, to atmospheric air, or any of the gases. This inference is so evident, that we can scarcely hesitate in admitting the conclusion, that gases are solids rarified, and rendered elastic by caloric.

The proposition is farther established by experiment. Two aëriform bodies in combining frequently form a substance which exists in the liquid or solid form; and in this case the caloric, to which they owed their aëriform state, is disengaged. And, by very intense colds, aided by compression, some gases which formerly appeared to

be permanently elastic, have been brought to the liquid state. This result has been obtained from oxymuriatic gas and sulphurous acid gas *. The objection, therefore, sometimes urged against the modern system of chemistry, that the principal substances whose actions it endeavours to trace are hypothetical elements, is founded on limited and superficial views.

The opinion of some, that the difference between the gases and the vapours consists in the combination of the caloric with the gravitating matter of each, being more intimate in the one than the other, is established by no evidence. It is deduced solely from these gases being in-condensable; but this is plainly owing to the low temperature at which these substances pass into the aërial form.

The established chemical nomenclature is founded on these views of the nature of the aëriform state. Every air or gas is considered as a solid substance, brought into the aërial form by the agency of caloric. This cannot be obtained solid and insulated, because we are unable to produce a reduction of temperature sufficient to abstract the caloric which adheres to it. But there is no doubt of its existence. The specific properties of the gas are considered as depending upon it; the form only being owing to caloric; and when it passes into chemical combinations, it is this matter which is considered as the agent concerned, as exerting those attractions from which the combination arises. In the usual nomenclature, the name of the gas is derived from this solid gravitating matter which is its base. Oxygen is thus spoken of as the base of Oxygen Gas; Hydrogen of Hydrogen Gas; and a similar nomenclature is extended to all the other airs.

The transition of bodies to the aëriform state is much influenced by pressure. This resists their expansion, or

* Experiments by Mr Northmore, Nicolson's Journal, vol. xiii.

the repulsion established between their particles, and hence, to convert a liquid into vapour, a higher temperature is requisite when pressure is present than when it is removed. Under the usual atmospheric pressure, water boils at 212° of Fahrenheit; but it undergoes the same change at 180° , or even some degrees lower, in the imperfect vacuum of the air-pump. At different barometrical altitudes it boils at different temperatures; at that of 26, for example, it boils at 205° *. Ether, which requires a temperature of 104° , boils rapidly in the exhausted receiver of the air-pump at the common temperature of the atmosphere. Quicksilver even, there is reason to believe, passes into vapour *in vacuo*. Pictet remarked, that when the barometer is exposed to considerable changes of temperature, occasionally to the solar light for example, very small drops of quicksilver collect in the upper part of the tube, which increasing, fall back into the fluid beneath †. And Roy observed the volatilization of quicksilver in the tube of the barometer, when the temperature was raised 20 or 30 degrees of Fahrenheit above a medium natural temperature ‡. It is doubtful, therefore, if even the Torricellian vacuum is a perfect one.

* This had been repeatedly employed as a method of measuring heights. And lately an apparatus has been constructed by Mr Wollaston for this purpose, portable, and of very considerable delicacy, so as to be equal to the common barometer. It consists principally of a thermometer having a very fine stem, with a large bulb, and with the scale adapted only to the short range of temperature that may be expected to require measurement. The degrees are thus very large, so that the smallest differences are apparent. The instrument is connected with a small apparatus, by which water may be made to boil, and the bulb of the thermometer be properly immersed. Philosophical Transactions 1817.

† Essais de Physique, p. 154.

‡ Philosophical Transactions, vol. lxvii, p. 670.

Pressure has an equal effect in repressing the elasticity of vapour, and by applying it in sufficient force the vapour is entirely condensed.

It thus appears, that the change of a fluid into vapour takes place through an extensive range of temperature, less being formed as the temperature is low. Nor is it solely dependent on temperature, but on temperature modified by pressure; so that the pressure varying, while the temperature remains the same, or the temperature varying while the pressure is constant, variable quantities of vapour are formed. Hence the amount of elasticity from a vapour, arising from a liquid under these different circumstances, is very different, as different quantities of it pass into that state. This subject has been investigated by Mr Dalton; and from an extensive series of experiments, he has ascertained the elastic force exerted by vapours in contact with the fluid from which they arise, measured by the column of mercury they sustain, through an extensive range of temperature.

Thus the vapour of water, in contact with water, sustains, at the temperature of 212° , a column of mercury of 30 inches; at 122° , it is equal to that of 3.5 inches; and at 32° , to .02 inch. Mr Dalton having observed a geometrical progression in the numbers, which, according to his experiments, expressed the elastic force of steam at different temperatures between 32° and 212° , the ratio being a gradually diminishing one, was enabled to fill up by interpolation, those degrees which he had not ascertained by actual experiment, and to extend a table of these forces at both extremes, that is, below 32° , and above 212° ; the ratios for each interval of $11\frac{1}{4}$ degrees below 32° , being 1.500, 1.515, 1.530, 1.545, &c.; and the ratios for each interval above 212° , being 1.235, 1.220, 1.205, 1.190, 1.175, 1.160, 1.145, 1.130, &c. On this principle, he constructed a table of the force of vapour from water, in every temperature from below 0 to

325°. It will be sufficient, instead of the full table, to give the numbers to every tenth degree *.

Tempe- rature.	Force of Vap. in inches of Mercury.	Tempe- rature.	Force of Vap. in inches of Mercury.
-40° — — —	.013	150° — — —	7.42
-30 — — —	.020	160 — — —	9.46
-20 — — —	.030	170 — — —	12.13
-10 — — —	.043	180 — — —	15.15
0 — — —	.064	190 — — —	19.00
10 — — —	.090	200 — — —	23.64
20 — — —	.129	210 — — —	28.84
30 — — —	.186	220 — — —	34.99
40 — — —	.263	230 — — —	41.75
50 — — —	.375	240 — — —	49.67
60 — — —	.524	250 — — —	58.21
70 — — —	.721	260 — — —	67.73
80 — — —	1.00	270 — — —	77.85
90 — — —	1.36	280 — — —	88.75
100 — — —	1.86	290 — — —	100.12
110 — — —	2.53	300 — — —	111.81
120 — — —	3.33	310 — — —	123.53
130 — — —	4.34	320 — — —	135.00
140 — — —	5.74	325 — — —	140.70

From this table we discover what quantity of vapour is produced from water at a certain temperature, measured by the column of quicksilver it sustains; water, for example, at a medium temperature, that of 50° of Fahrenheit, giving vapour which sustains a column of 0.375 inch; and hence also we discover at what temperature, and under what pressure, vapour will be formed. Thus, at 50° it is produced, when the pressure is that which has just been stated, 0.375 inch of mercury. It is not to be conceived, as it might be from the way in which the fact is expressed, that, under these different circumstances, the same quantity of vapour passes into vapour, and that

* Manchester Memoirs, vol. v, p. 559.

this vapour has more or less elasticity; but that different quantities of it pass into that state; the quantity being greater at a given temperature, as the pressure is less, or under a given pressure, as the temperature is high; and hence the exertion of a greater elastic power; in other words, the increased elasticity of vapour in contact with the liquid affording it, as the temperature rises, is owing to a larger quantity of liquid passing into that state, and, of course, under a given pressure, to the steam being more dense at a high than at a low temperature.

Other experiments, on the force of watery vapour, at different temperatures, particularly those by Bettancourt, which are the most extensive, and perhaps the most accurate, give numbers somewhat less in the lower part of the scale, and greater in the higher, as is apparent from the following table, in which the force of vapour, every ten degrees of Reaumur's scale, is expressed by the column of mercury measured by inches, which it sustains*.

Temperature. Reaumur.	French inches.	Fahrenheit.	English inches.
0	0.00	32	0.00
10	0.15	54.5	0.16
20	0.65	77	0.69
30	1.52	99.5	1.62
40	2.92	122	3.11
50	5.35	144.5	5.71
60	9.95	167	10.61
70	16.90	189.5	18.02
80	28.00	212	29.86
90	46.40	234.5	49.49
100	71.86	257	76.57
110	98.00	279.5	104.52

It is remarked by Mr Dalton, that the assumption of the force of vapour at 32° of Fahrenheit being nothing renders the numbers incorrect in the lower part of this

* Journal Polytechnique, cahier ii, p. 47.

scale ; and that in the higher part they are represented as too great, owing, as he supposes, to a portion of air being disengaged from water by heat mixing with the steam, and augmenting its elasticity. . Any deviation from this cause, however, must be extremely trivial · when care is taken even to obviate it, little difference is found, and as this inconsiderable disengagement of air will always take place in actual experiment, in the application to practical purposes, to calculating, for example, the force of steam, as a mechanical power, the numbers deduced in this way are to be preferred ; and they derive considerable authority from resting on actual experiment.

Mr Dalton extended his experiments to other liquids, and, as the result of them, inferred the general law, “ That the force of vapour from all liquids is the same, at equal distances above or below the several temperatures at which they boil in the open air.” Thus, the elastic force of the vapour of water heated to 212° , is equal to a column of mercury 30 inches in height ; by a diminution of 30 degrees of temperature, its elasticity is diminished one-half ; hence, according to this law, the vapour of any other liquid must lose half its force, by a diminution of temperature equal to 30 degrees below that at which it boils under a common atmospheric pressure ; and the like for any other increment or decrement of heat. The elastic force, therefore, of the vapour of water at different temperatures being determined, it is easy to find that of any other liquid, the boiling point of which is ascertained ; the elasticity of the vapour of that liquid, at any distance from its boiling point, being the same as the elasticity of the vapour of water at the same distance from *its* boiling point. The boiling points of ether, according to Dalton, being 102° , of alkohol 175° , of liquid ammonia 140° , of liquid muriate of lime 230° , the force of the vapour of each, at 60° , is as follows : that of ether is equal to 12.13 inches of mercury ; that of alkohol 1.5 ; that from liquid

ammonia 4.3; that of the vapour from liquid muriate of lime, about 0.26 of an inch *. This law, however, is doubtful, and it leads to some conclusions which appear not to be just, with regard to the force of vapour at different temperatures from different bodies †.

In Mr Dalton's experiments on the elastic force of steam arising from water, it appeared that the force increases *nearly* in a geometrical progression to equal increments of temperature, as measured by the common mercurial scale. It will be *precisely* geometrical, he has since remarked ‡, if the increments of temperature are measured by a thermometer, the scale of which is divided, according to the law, that the expansion of the thermometrical fluid is as the square of the temperature from its freezing point; and he has farther inferred, that all vapours from pure homogeneous liquids, in contact with their respective liquids, increase in geometrical progression to the increase of arithmetical temperature,—conclusions which rest on the truth of this law, which is extremely doubtful. Where the liquid is not homogeneous, the progression is not geometrical, as the vapour is a mixture of the substances composing the liquids. This is the case with alcohol, which always contains a mixture of water; and as this is various, the force of vapour from it is not easily ascertained with precision. The experiments of Bettancourt give results somewhat different from Dalton's; the proportion in its force to that of watery vapour being stated, at all temperatures, as more than double, or as 7 to 3 nearly §.

The younger Saussure has stated a law which appears to exist with regard to the specific gravities of vapours, in

* Manchester Memoirs, vol v, p. 563. &c,

† Young's Natural Philosophy, vol. ii, p 398.

‡ New System of Chemical Philosophy, p. 10, 13.

§ Journal Polytechnique, cahier ii, p. 48, 49.

relation to the volatility of the liquids from which they are formed,—that they are less as the fluid is less volatile. Water is less volatile than alkohol, and alkohol is less volatile than ether; but the elastic vapour of water is lighter than that of alkohol, and the vapour of alkohol is lighter than that of ether. He infers, therefore, that the specific gravity of vapours is in the direct ratio of the volatility of the liquids that afford them. Hence an inference, rather singular, that if elastic fluids, when presented to each other, did not remain diffused, but arranged themselves according to their specific gravities, of the vapours arising from the surface of the earth, those from the least volatile bodies, as the metals and earths, would be those which would occupy the higher regions of the atmosphere, supposing that its temperature were uniform *.

By increasing pressure on fluids, they may be heated to a very high temperature. In Papin's digester, a close iron vessel in which, by means of a valve on which a regulated weight presses, vapour may be retained to a considerable extent without bursting the vessel. Water has thus been heated to above 400° , and, by this increase of temperature, its solvent power with respect to many substances is much increased.

The transition of substances into vapour is considerably accelerated by passing over the surface of the body heated a current of air. It had been known, that if a liquid be exposed to a moderate heat in a vessel, having an imperfect communication with the air, it evaporates slowly, while it evaporates rapidly at the same temperature under a free exposure to the air; and also, that in decomposing one body by another, the decomposition, when accompanied with the expulsion of an elastic product, does not proceed so rapidly in vessels close or partially closed, as when the mixture is exposed to the air. This has been more fully

* Nicolson's Journal, vol. xxi, p. 336.

investigated by Guy-Lussac *. If sulphuric acid be poured on nitre, vapours of nitric acid continue to be disengaged for a long time under exposure to the air; but they soon cease if the air is excluded. If muriate of potash, and indeed a number of salts, be kept in fusion in an open vessel, there is a loss of weight, which does not happen if the vessel be lightly covered; and if the cover be removed, vapours almost immediately arise, though none appeared to escape before from the small apertures at the sides of the cover. A number of the metals, too, lead, antimony, and bismuth, give fumes at a red heat in an open crucible, but afford no sublimate in a closed crucible; appearing, therefore, to be in the one case volatile, in the other fixed. Lastly, water evaporates at a common temperature if exposed to the air, but cannot be distilled at the same temperature in vessels imperfectly closed. The principle by which Gay-Lussac accounts for these facts, is one advanced by Mr Dalton, that the transition of a liquid into vapour at temperatures inferior to its ebullition, is not counteracted by the pressure of a different elastic fluid, but only by the pressure of its own vapour. In a vacuum, for example, a portion of water passes into vapour, and this vapour exerts a certain elastic force, regulated by the temperature which limits the quantity evaporated. The same quantity of vapour, Mr Dalton assumes, will arise from water and exist in the same space, although that space be occupied by a different elastic fluid. The transition of a body into vapour, therefore, will go on in atmospheric air as it would *in vacuo* at the same temperature: it is only when the vapour is kept in contact with the body that the evaporation is counteracted, and hence the reason why that evaporation is suspended in vessels which are closed, or have an imperfect communication with the atmospheric air. It may be doubted, however, if the principle on which

* Mémoires d'Arcueil, tom. i, p. 204.

this explanation rests is just, and the effect of atmospheric air or of any other elastic fluid in promoting the transition into vapour is probably owing to the affinity it momentarily exerts to the body evaporating at the surface at which the evaporation takes place.

Bodies passing into the aëriform state absorb a large quantity of caloric, which does not increase their temperature. The consideration of this important phenomenon will be introduced with more advantage, in connection with another subject—the quantities of caloric which bodies contain.

FROM the different tendencies which bodies have to pass into vapour, we are enabled to separate them from each other when they are previously combined, or when they become products of chemical action; and peculiar arrangements, adapted to different cases, being requisite for this purpose, constitute several chemical operations relative to vaporisation, which, with the apparatus in which they are performed, fall to be described under this part of the subject.

When heat is applied to recover a solid substance dissolved in a fluid, without any arrangement being made to preserve the fluid, the operation, which is named Evaporation, is performed in shallow vessels, which, presenting an extensive surface, admit of the liquor being quickly heated, and of the vapour escaping without any resistance. These vessels are of glass, earthen-ware, or metal, according to the nature of the substances operated on, and the degree of heat which is to be applied. In chemical experiments on a small scale, basons of glass, or of Wedgwood's earthen-ware, sometimes also of silver or platina, are used, the heat being applied by the medium of a sand-bath. In pharmacy and the arts, they are constructed of iron or lead, and the heat is directly applied. Rumford has endeavoured to determine the capacity of boilers, best

adapted to the evaporation of water, from a given quantity of fuel ; and the same problem has been made the subject of experiment by Hassenfratz, who has added some experiments on the comparative results of evaporation at different temperatures. The result with regard to the last, is, that it is most economical to keep the liquor up to its boiling point, the greatest quantity being thus evaporated with the least consumption of fuel *. At the same time, it is often necessary not to raise the heat too high, as the vapour, by its affinity to the fixed body, elevates part of it with it in a combined state. This has been found to be the case with regard to the most fixed salts, when water is evaporated from them at a high heat.

When the object is to obtain the volatile matter by evaporation, it is carried on in close vessels, constructed so as to collect and condense the vapour. The operation is named Distillation. Different kinds of distilling apparatus are employed, adapted to different purposes.

Where the process is conducted on a large scale, as in the distillation of ardent spirits, the common Still, made usually of copper, is employed. It consists of a large body somewhat cylindrical, which contains the liquor ; a head is adapted to it with a curvature, which is connected with a spiral tube, or worm, as it is called, placed in a vessel of water named the Refrigeratory ; the vapour arising from the liquor, when heat is applied by a furnace to the body of the still, rises into the head and passes into the spiral tube, where it is condensed, and is collected at its extremity. The construction of the common still has usually been very imperfect. The body being of a considerable height proportioned to its diameter, a large mass of liquor is to be heated, while comparatively a small surface is exposed to the fire, and hence a waste of heat. And the tube issuing from the head of the still, conveying the vapour into the

* Journal Polytechnique, cahier vi, p. 364.

spiral tube placed in the refrigeratory, being generally narrow, the vapour is accumulated, and by its pressure on the liquor retards the evaporation. In this country the construction of the common still has, within these few years, received very great improvements, by the skilful application of the principles which regulate distillation. The height of the still of the new construction is inconsiderable, compared with its diameter, and by the width of the tube a free escape is allowed to the vapours; hence the distillation can be performed with a rapidity which would formerly have been thought impracticable*.

Another improvement is that of the double still by Mr Tennant, in which the spiral tube from one still is introduced into the body of a second still, so that the heat from the condensation of the steam passing through the tube shall be applied to the distillation of liquor contained in the second. This is effected by removing from the latter the pressure of the atmosphere, by connecting it with a receiver made air-tight with a stop-cock adapted and kept cool. The air in the receiver being allowed to escape at the commencement of the operation, its place is occupied by the steam from the liquor, the boiling of which has been accelerated by heat directly applied; and this being condensed by the cold, a vacuum is kept up, which allows the distillation to proceed at the heat produced by the condensation of the steam from the first. About three-fourths of the quantity obtained by the first distillation are thus added by the second†. Another method, somewhat similar, but more simple and more easily managed, is that of applying the heat given out by the condensation of vapour in distillation to raise the temperature of the portion of liquor which is next to be distilled. This is done by in-

* Report on the Scotch Distillery, Philosophical Magazine, vol. vi, p. 70.

† Philosophical Transactions, 1818, p. 588.

terposing a closed vessel between the head of the still and the worm of the refrigeratory, in which a wide tube or cylinder connecting these is placed; the vessel is nearly filled with the liquor intended to be distilled, and the heat from the vapour passing through the tube and condensing elevates its temperature so far, that in transferring it to the still there is a considerable saving of fuel. A patent still of this construction has been pretty extensively used in some of the West India islands *.

It is an object of importance in the distillation of vegetable substances with water or spirit, to avoid empyreuma from too strong a heat being applied, or from the matter adhering to the bottom of the still. A patent has lately been taken for a still, for the distillation of spiritous liquors, having this advantage. The still is placed within a vessel containing water, to which the heat is applied, and is connected with condensing receivers, cooled in the usual manner, which are exhausted, so that a comparatively low heat, applied by the medium of the water, is sufficient for the distillation †.

In the greater number of chemical operations, metallic vessels are acted on either by the materials, or by the product of the operation; hence glass-vessels generally require to be employed in distillation. The Retort or conical bottle, the neck of which is bent at an angle of about 60 degrees A, adapted to a receiver B, (Fig. 31, Plate III.) is the most convenient apparatus of this kind. Sometimes it is convenient to have it tubulated, as in Fig. 32. A, and also to have the distance between it and the receiver increased, so that the latter may be kept sufficiently cool, by an intermediate tube B, or Adopter as it is named. The heat is applied by the medium of a water-bath or sand-bath. Sometimes it is made of earthen-ware, where

* Repertory of Arts, NO. 132.

† Annals of Philosophy, vol. xi, p. 445.

it is designed to be exposed to a very intense heat; and it is covered with a coating of clay and sand when the fire is to be immediately applied to it.

In some cases of distillation, the product is not entirely a vapour, which may be condensed, but there is likewise disengaged an elastic fluid, which is incondensable. The receiver having a bent tube issuing from it, represented by C, Fig. 32, is employed in this case; the condensable part of the product is collected in the body of the receiver, and the elastic product issuing through the tube, which terminates in a vessel of water, may be collected in an inverted bottle or jar.

In certain cases, the elastic product is not condensable by itself, but is capable of being condensed by being transmitted through water, with which it combines. The apparatus invented by Woolfe, Fig. 33, is employed for this purpose. It consists of a series of bottles, A, B, C, D, connected with each other by bent tubes, and connected with a retort generally by the medium of an adapter. The first bottle A is designed to collect any condensable part of the product. In the other bottles, water is placed to nearly one-half their height, represented in the figure by the dotted line, and the tube passing from the one into the other, beyond the second bottle B, dips into the water of the bottle into which it is inserted, as is represented in the plate. The gaseous product is thus transmitted through the water, and is absorbed by the affinity exerted to it by the water, aided by the pressure of the short column of water in each tube; if any portion is incapable of being absorbed by the water, it passes off by the bent tube at the end, and may be collected in an inverted jar, in a trough of water. Each of the bottles except the first has a straight tube, which rises to the height of 8 or 10 inches above its insertion into the bottle, and passes so far within it as to dip in the water nearly half an inch. This is termed the tube of safety, and the use of it is to guard

against that reflux of fluid which might happen from a partial vacuum arising from condensation in any of the bottles; for as the air in the bottles is expelled at the commencement of the distillation, by the gas produced, if the production of gas should diminish, the quantity contained in the bottles being absorbed by the liquor, a partial vacuum is formed, and at the end of the process, when the retort cools, this must always happen; the consequence is, that the water being more pressed on by the atmospheric air without, than by the gas within, passes backwards from one bottle to another, by rising through the tubes, as from D to C and from C to B, and thus the whole is mingled together, defeating the object of distillation. This is prevented by the tubes of safety, as when any such partial vacuum happens, the atmospheric air is forced through the small quantity of fluid in which they are immersed, and rising into the bottles, preserves the equilibrium.

Various improvements have been made in this apparatus. One defect in it is, that we cannot have the advantage of the immersion of the tube which comes from the first bottle A into the liquid in the second B; for as A is designed to collect the condensable product, and ought therefore to be without water, it can have no tube of safety; and hence, if the tube issuing from it dip into the liquid in the second, whenever condensation happens, the liquor will pass backwards into it. The apparatus, therefore, is represented in the plate, with the bent tube from the first bottle reaching near the surface only of the liquid in the second, while in all the others it is immersed. As the liquid, however, in the second bottle, is in the best situation for being impregnated with the gas, and therefore for forming the most concentrated product, it is of importance to aid this, and obtain the advantage of the gas being forced to pass through it, by the tube being immersed. The contrivance that has been used for this pur-

pose is the tube of safety of Welther, or bent tube with an additional curvature, and a spherical ball, represented A Fig. 34, as intermediate between the globular receiver and the common Woolfe's bottle, and connecting them. In this is put a small quantity of water, so as to rise, when the pressure without and within is equal, about half way into the ball. If the elasticity is increased in the internal part of the apparatus, during the distillation, by the production of gas, the water is pressed upwards to the funnel at the top; if there is a condensation, it is forced by the atmospheric pressure into the ball, but whenever it has passed the curvature beneath the ball, it is obvious that a portion of air must rise through it, and will pass into the globe or bottle. This tube, however, from its form, is very liable to be broken; and no great pressure can be employed with it, without making it of such a length as to be unwieldy and subject to risk. The method I employ to obviate this inconvenience is more simple. It is having the usual bent tube constructed with a ball, in that part of it which is inserted in the bottle B, containing the liquid into which it is to dip, as represented Fig. 36. By proportioning the depth to which the tube is immersed in the liquid in B, to the size of the ball, it is obvious, that when the ball is filled from the liquor rising into it, the extremity of the tube will be no longer immersed; a portion of the gas will rise through the liquor into A, and preserve the equilibrium. This method has the advantages that we can employ any pressure in the apparatus, and that no atmospheric air is introduced in the course of the distillation into the first bottle, but only the elastic fluid which is the product of the process. The adaptation of tubes of this kind to all the bottles, may even supersede the use of tubes of safety through the whole apparatus; while any extent of pressure may be obtained by immersion of the tube from the last bottle in the requisite depth of water or quicksilver.

Another imperfection which attends the common Woolfe's apparatus, is the difficulty of adapting the tubes by grinding, so that it is necessary to secure the joinings by lute, which is always inconvenient. The method I have employed to remedy this, is by having a tube fixed when the bottle is made, into that orifice into which the long leg of the tube from the preceding bottle is to enter, as represented Fig. 36, in the bottles B, C, D. This wide tube being of such length that it is immersed in the liquor within the bottle, and the tube which enters it having a very slight curvature at its extremity, the gas which it conveys is propelled forward, rises through the water, and passes into the next bottle; and as there is no difficulty in grinding the tubes into the bottles *from* which they issue, the whole apparatus is easily constructed without the necessity of lute. The open tube, too, serves the purpose of a tube of safety. In this apparatus, however, little pressure can be applied to promote the absorption of the gaseous product, as, from the shortness of the open tubes, the liquor, by such a pressure, is forced up, and may overflow, but this may to a certain extent be obviated, by having the open tubes not fixed, but fitted by grinding, and having them of such a length as will admit of the rise of the liquid, as is represented in E. Other improvements of the original apparatus have been proposed,—one by Mr Burkitt*, in which a valve is introduced; one of a similar kind by Mr Pepys, and another by Mr Knight†.

What, upon the whole, however, will be found the most convenient apparatus, is one described by Dr Hamilton, in his translation of Berthollet's Treatise on Dyeing, represented with some variations, Fig. 37. It consists of a series of globular vessels, which are fitted by grinding to each other. The first is inserted into the second by a

* Nicolson's Journal, 4to, vol. v.

† Philosophical Magazine, vol. xx.

short neck, for the reason already stated, that, being designed to receive the condensible product, water cannot be put into it at the commencement of the distillation, and therefore a tube of safety cannot be inserted. From the second, there passes a tube, having such a curvature that it can be easily introduced into the third, and be immersed in the water which it contains; the third has a similar curved tube, which passes into the fourth, and the fourth terminates by a bent tube in a small pneumatic trough *. In the second bottle is inserted a tube of safety. In the other bottles this is not necessary, as the condensation in them is never considerable. The great advantages of this apparatus are, that all the parts of it can be easily adapted by grinding, and that it is not liable to be broken by any slight dislocation,—advantages which cannot be obtained when the tubes are bent as in the common apparatus. The only deficiency is, that as the tubes cannot have such a curvature as to be made to dip more than an inch in the water, the degree of pressure cannot be great, so as to facilitate the absorption of the gas. But this may be obviated by connecting with the last bottle, where it is required, a tube bent at right angles, like the common bent tube of the Woolfe's apparatus, which is immersed in a jar of water to the depth that may be required; and by substituting quicksilver for water in this jar, any pressure that the apparatus can sustain may be obtained.

There is one other form of the pneumatic distilling apparatus, invented by Dr De Butts of Baltimore, which is possessed, independent of its general use, of a particular advantage. It consists (Fig. 35.) of two or more bottles.

* In the original apparatus, these curved tubes are adapted to the necks of the globes, by grinding; but this is unnecessary, as the globe can be easily made with the tube projecting from it.

The first A is connected by a tubulature towards the top with the tube of a retort, or an adopter; nigh the bottom, on the opposite side, is another tubulature, and in the next bottle B, at the same height from the bottom, is a similar opening; these are connected by a straight tube without, which has such a curvature within the bottle A, as to rise above the water employed to condense the gas, the surface of which is represented by the dotted line: the succeeding bottles are connected in a similar manner. It is obvious that the gas passes forward through the bent tube, and is transmitted through the water in the next bottle; the tubes may be fitted by grinding, but it is difficult to have this done with perfect closeness; they may therefore be inserted by corks waxed; and as these are not exposed directly to the gas, but are under the liquid, they will in general be little acted on. Tubes of safety are adapted in a similar manner; and as it is inconvenient to detach the bottles, the liquor, when the distillation is completed, may be drawn off by a syphon inserted by the orifice at the upper aperture, or by an aperture in front at the bottom, fitted accurately with a stopper. The peculiar advantage of the apparatus is, that all the joinings, with the exception of the first, are under water, and the gas therefore cannot escape. Hence, in distillations in which the product is peculiarly offensive, as in that of oxymuriatic acid, it affords the best security against any noxious effect.

A liquid obtained by distillation is sometimes not perfectly pure, or it is dilute from the intermixture of water that has risen in vapour with it. By repeating the distillation a second or third time, it is rendered more pure and strong: the process is then named Rectification, or sometimes Concentration.

When the product of volatilization condenses in the solid form, the process is named Sublimation; and as such products are in general easily condensed, a simple

apparatus only is required. The alembic with its capital, Fig. 38. Pl. IV. is generally used. The alembic A is a conical shaped vessel of glass, in which the materials are put, and exposed to heat in a sand-bath, the sublimate condensing in the upper part of it, and forming a crust on its sides. The capital B is adapted to its mouth to prevent the escape of the vapour; a small groove or channel runs in the under part, terminating in a tube projecting from it, by which any liquid is collected and prevented from running down or dropping on the sides of the alembic.

I have, lastly, to take notice of the apparatus requisite for operating on bodies which are permanently elastic.

The principal part of this apparatus is the Pneumatic Trough, invented by Priestley. It is a trough of wood, lined with lead, generally of an oval form, about 8 inches deep, from 20 to 24 in length, and at the greatest breadth 15 inches; a moveable shelf being placed in it, at the depth of 2 inches from the edge, in the longest direction, so as to occupy one-half of the breadth, as is represented in Fig. 46. If a glass jar filled with water be placed inverted on this shelf, the trough being filled with water to the edge, it is obvious that the water within it will be sustained by the pressure of the atmosphere. If the extremity of a retort, or tube connected with a bottle disengaging gas, be placed under it, or if another inverted jar, containing any air, be turned up, under the mouth of it advanced a little over the shelf, the elastic fluid will rise through the water, displace it, and be collected in the jar; and while the mouth of this jar continues surrounded with water, the included air cannot escape, nor will the atmospheric air find access to it. In this way, æriform fluids can be collected, preserved, and submitted to experiment. Some of them, however, are rapidly absorbed by water. These must be received and kept over quicksilver; and as this fluid is expensive, and inconvenient from its weight, a

smaller trough is employed, either hollowed out of marble, or of a solid block of hard wood. This is represented Fig. 47, with an addition which is convenient,—a small rod fixed in the wooden standard on which the trough is placed, which by a ring attached to it by a sliding arm, serves to support, without any risk, the jar filled with quicksilver, and placed on the shelf. Various other forms of this apparatus, designed principally to lessen the quantity of quicksilver, are in use.

The other principal part of the apparatus, for operating on the gases, is the Gazometer, designed to contain gases, so that measured quantities can be withdrawn. The forms are various: one of the most simple, and which answers sufficiently for all common experiments, is that represented Fig. 48. It is made of tinned iron, the surfaces of which are japanned, and consists of two principal parts; a vessel A, somewhat bell-shaped, which is designed to contain the gas, and a cylindrical vessel of rather greater depth, B, in which the former is placed, and which is designed to contain the water by which the gas is confined. To diminish the quantity of water, this cylindrical vessel has a cone within it, also of japanned tinned iron, C, adapted to the shape of the gas-holder, so that this latter, when pushed down, slides between this and the cylindrical vessel, and a small quantity of water fills up the space between them. The vessel designed to contain the gas is suspended by cords hung over pulleys, to which weights are attached so as to counterpoise it. From a stop-cock at the under part of the apparatus, D, there runs a tube under the cylinder, which rises through the centre, passing through the cone, the opening by which it passes being soldered so as to be air-tight, and terminating by an open mouth at the upper part of the bell-shaped vessel A. This tube, at the part where it is bent at right angles, to ascend, is connected with another which also runs under the bottom, and ascends on the outside, terminating in

the stop-cock E, so that from the one stop-cock to the other, through the gas holder, there is an uninterrupted passage. When the instrument is to be used, the stop-cock E is opened, and the vessel A is pressed down, a sufficient quantity of water being in the outer cylinder; the air of the vessel is forced out by the pressure, and its place is occupied by the water in which it is thus immersed. The stop-cock is then closed, and to introduce any gas into the apparatus, a bent funnel, the mouth of which is placed in a vessel of water, is attached to the tube of the stop-cock D, as represented in the figure, and the stop-cock is opened: if the extremity of a retort, or of a tube, conveying gas, as represented in the figure, terminate below the orifice of the funnel, the gas will rise along the tube, will ascend to the top of the gas-holder, and this being counterpoised, will, as the gas enters, rise in the water until it is filled, a quantity of water remaining around the mouth of it, by which the gas is confined. When we wish to expel the gas, the stop-cock at D is closed, that at E is opened, a flexible tube is adapted to it, and the gas-holder being pressed down, either by the hand, or by its own weight from the removal of the counterpoising weights, a stream of gas issues from the extremity of the flexible tube, and may be transferred into a jar, or be applied to any other purpose; and its quantity may be measured by the instrument being graduated by a scale marked on the brass rod F.

The instrument connected with the gazometer in the plate, Fig. 49, is a convenient one for procuring gases from any solid substance, by a strong heat. It is an iron bottle A, into which is fitted, by grinding, a tube bent at an acute angle. To this a smaller tube is adapted, the extremity of which can be adapted to various heights, by a circular joint in the middle of it, at *b*. The bottle containing the materials from which the elastic fluid is to be disengaged is placed in a furnace, or in a common fire,

so as to be raised to a sufficient heat, the gas issues at the extremity, and may be conveyed into the gazometer, or received in an inverted jar on the shelf of the pneumatic trough. At the end of the operation, the gas ceasing to be produced, as the heat diminished, the water would rise in the tube, and might pass into the bottle. The easiest way of obviating this, is by having a small stop-cock in the tube as at *c*, which may be opened when the production of the gas has ceased.

When a gas is extricated, in consequence of chemical action, with the application only of a moderate heat, the flask or cucurbit, with a bent tube ground to it, Fig. 45, is the most convenient.

In all accurate experiments on gases, it is of importance that the quantities should be determined with precision. The absolute quantity is best determined by introducing the gas into an exhausted flask of known capacity, and weighing it in a delicate balance. The specific gravity is found reduced to atmospheric air, by comparing the weight with the weight of atmospheric air introduced into the same vessel previously exhausted; and the weight of 100 cubic inches of atmospheric air, under a mean pressure and temperature, being 31 grains, the weight of 100 cubic inches of the gas submitted to experiment may be thus found; that is, as the weight of the air in the flask is to 31, so is the weight of the gas in the flask to the weight of 100 cubic inches of it.

To weigh the gases requires, however, a very delicate and complicated apparatus: chemists estimate, therefore, usually, their volumes, and find their weights by a reference to the tables of their specific gravities, which have been constructed. Hence jars graduated into cubic inches and tenths are convenient, as are also, in other cases, jars graduated into equal arbitrary parts, to determine relative results. In thus estimating the weights of gases from their volumes, several circumstances require to be

attended to, particularly the temperature and the pressure. Elastic fluids being so expansible, a considerable change in their specific gravity is made, by a trivial alteration of temperature. The standard temperature of 54.5 of Fahrenheit is assumed as that at which the specific gravities of the gases are ascertained, and if their temperatures are different from this, the due correction is to be made. The following is the formula. Aëriiform fluids are expanded $\frac{1}{480}$ of volume by each degree of elevation of temperature, according to Fahrenheit's scale. Divide therefore the observed volume of gas by 480, and multiply the quotient by the number of degrees at which the temperature of the gas is either above or below 54.5 of Fahrenheit. The correction is negative when the actual temperature is above the standard, and positive when it is below it. In the former case, therefore, the product of the multiplication is to be subtracted from the observed volume; in the latter it is to be added to it, to give the real volume*.

The other correction that may be requisite is, any varying pressure, whether of the atmosphere, or of any fluid in which the vessel containing the gas may be more or less immersed. The weight of the gases is fixed at the mean barometrical pressure 29.85 inches of mercury; and if the atmospheric pressure be different from this, the correction must be made to bring it to the standard. The volume of all elastic fluids is in the inverse ratio of the

* The above formula is that given by Lavoisier, substituting only $\frac{1}{480}$, for $\frac{1}{477.3}$ as the expansion of the gas. It is not, however, perfectly correct in reducing from a higher to a lower temperature, for the volume in the higher temperature is greater than that at the lower, and therefore the part $\frac{1}{480}$ in the one is different from that in the other. As the correction, however, seldom extends to an interval of temperature more than 10 degrees, the error is so trivial that it may be neglected.

weight compressing them. As the mean barometrical pressure, therefore, is to the actual pressure, so is the observed volume to the volume at the mean pressure. If, for example, the observed volume of a gas at the standard temperature 54.5 is 100 cubic inches, the barometer being at 30.37, to determine what volume it would occupy at the mean barometrical pressure 29.85, let x represent the unknown volume; then $100 : x$ inversely, as $30.37 : 29.85$, or directly, $29.85 : 30.37 :: 100 : x = 101.741$; or the gas, which at 30.37 barometrical altitude occupies 100 cubic inches of volume, will at 29.85 occupy 101.741. The simple formula therefore is, multiply the real pressure under which the gas is, by the volume of the gas: divide the product by the mean barometrical pressure, and the quotient is the volume under that pressure.

Another correction which may be requisite is, *that* from the pressure of the fluid surrounding the mouth of a jar containing air. If a jar containing air stand on the shelf of the pneumatic trough, and if the water, without and within the jar, be at the same level, it is obvious that the pressure is equal, and is merely that of the external atmosphere; but if it be surrounded without with water, to a greater height than that within, there is this additional pressure to that of the atmosphere on the included air; and if it were surrounded with quicksilver, as the weight of this is so much greater, the pressure must be more considerable: Or if the jar were only $\frac{3}{4}$ ths filled with air, the other fourth being filled with water or quicksilver, it is obvious, that this counteracts the pressure of the atmosphere on the gas included, and that the real pressure to which it is subjected is the atmospheric pressure *minus* the weight of the column, whether water or quicksilver, within the jar, which of course must be allowed for. The most convenient mode is to bring the fluid within and without the vessel to the same height; but this is not always practicable.

The following is the manner in which this is corrected, and the apparent volume brought to the real volume under a given pressure. When quicksilver is the fluid, measure the height of the column of it within the cylindrical jar, and subtract this from the observed barometrical pressure. Suppose that the height of the column of quicksilver is six inches, and that the barometer is at 30, this gives 24 as the real pressure under which the gas in the jar is. Measure the volume it occupies, which suppose to be 100 cubic inches. Then x representing the unknown volume, $100 : x$ inversely, as $24 : 30$, or directly $30 : 24 :: 100 : x = 80$ cubic inches, the volume of the gas when the barometer stands at 30. The simple formula therefore is, subtract the height of the column of quicksilver in the jar from the atmospheric pressure, as indicated by the barometer; multiply the remainder by the volume of gas; divide the product by the real barometrical pressure, and the quotient gives the volume under that pressure. Or, if the division be made by 29.85, the mean atmospheric pressure, this gives at once the volume of gas under that pressure. Thus, if in a cylindrical tube 15 inches long, a quantity of gas occupy a volume of seven inches, the other eight inches, being occupied by quicksilver, subtract the height of the column of quicksilver from the observed atmospheric pressure; suppose this to be 30 inches, this leaves 22, which is the real pressure under which the gas is. Multiply this by 7, the height of the column of gas, which gives 154. Divide this by the real barometrical height 30, and this gives 5.1, the volume of the gas under this pressure. Or, if we divide by 28.85, we have the volume under the mean barometrical pressure.

When water occupies the space in the jar, the calculation may be made from its specific gravity compared with that of quicksilver, the former being to that of the latter as 1 to 13.5: the depth therefore of $13\frac{1}{2}$ inches of water will reduce the volume of gas the same as an inch of mer-

cury does ; or an inch of water is equal in pressure to .0737 of an inch of quicksilver. The following short table is convenient for converting at once the observed heights of water, expressed in inches and decimals, to corresponding heights of mercury.

Water.	Mercury.	Water.	Mercury.
.1	.00737	4.	.29480
.2	.01474	5.	.36851
.3	.02201	6.	.44221
.4	.02948	7.	.51591
.5	.03685	8.	.58961
.6	.04422	9.	.66332
.7	.05159	10.	.73702
.8	.05896	11.	.81072
.9	.06633	12.	.88442
1.	.07370	13.	.96812
2.	.14740	14.	1.04182
3.	.22010	15.	1.11525

OF IGNITION.

THE effects arising from the operation of Caloric, hitherto considered,—Expansion, Fluidity and Vaporisation, are so far connected, that they appear as different degrees of one more general effect,—the increase which it occasions in the distances of the particles of bodies. Ignition cannot be referred to this cause. and is therefore an effect of caloric, having no apparent connection with the others.

By Ignition, or Incandescence, is meant that illumination or emission of light, produced in bodies by exposing them to heat, and which is not accompanied with any other chemical change in them. It is to be distinguished from combustion, a process in which there is also the emission of light and heat. Combustion is the result, not

of mere increase of temperature, but of the chemical action of the air, or of a principle which the air contains : a certain class of substances, denominated Combustible, are alone susceptible of it ; and when the process has ceased, the body remains no longer combustible. Ignition is an effect of the operation of caloric alone ; it is independent of the air, for by immersing any body in melted glass, it is rendered luminous ; all bodies, at least all solid and liquid substances, are susceptible of it ; and if it has ceased from reduction of temperature, it may be renewed by the temperature being raised.

The temperature at which the first stage of ignition takes place, or at which, in common language, bodies arrive at a red heat, appears to be the same in all. Mr Wedgwood gilded lines running across a piece of earthen ware, and luted it to the end of a tube, which was placed in a heated crucible ; the eye being applied to the other extremity of the tube, no difference of time could be perceived in either the gold or the earthen ware beginning to shine. No two substances can be more dissimilar ; and it may be inferred, that all bodies become red-hot at the same temperature. As this can be judged of only by the illumination, it must appear various, according to circumstances. In a body, which in the dark appears at a low red heat, the illumination will not be visible in day-light. Sir Isaac Newton, by observing the celerity with which a body cools, and calculating on the principle which has been already pointed out (p. 225,) concluded, that ignition, visible in the dark, corresponds with 635° of Fahrenheit's scale ; full red heat with 752° ; and ignition visible in day-light with above 1000° . Dr Irvine, having found that quicksilver boils at 672° , and that when boiling it does not appear luminous in the dark, it followed, that the point of ignition must be higher than Newton had supposed it to be. He had farther found, that when equal *bulks* of iron and water, at different temperatures, are

mixed together, the resulting temperature is nearly the *mean*, and he applied this method to determine the point of ignition : the result is not precisely known ; but the heat of a common coal fire he found to be 790° or 796° *. Mr Wedgwood, by the expansion of the piece of silver, measured by a gage of baked clay, by which he endeavoured to connect his thermometer with that of Fahrenheit's, as has been already explained, fixed the point of ignition visible in the dark at —1 of his scale, corresponding with 947° of Fahrenheit ; and ignition, in day-light, he placed at the commencement of his scale, or 1077° . This, it has already been remarked, there is reason to believe, is too high ; and independent of other circumstances it is probable that the silver would suffer an increasing expansion, which would cause the temperature to appear higher than it actually was. The lowest point of ignition is probably not far from 800° of Fahrenheit.

By raising the temperature, the illumination becomes brighter, and the red heat acquires a mixture of yellow rays. At length, by increasing the heat, we have the due proportion of coloured rays, which forms perfectly white light. This is the highest state of ignition, any farther rise of temperature producing no apparent change.

Ignition continues undiminished, as long as the temperature is kept up, unless the heat be such as to volatilize or alter the constitution of the ignited body.

The aëriform fluids are not brought into a state of illumination by heat. This was observed by Dr Fordyce, in the example of the vapour, at the end of the flame of a blow pipe, which though itself not visibly luminous at its extremity, will, if applied to glass, raise it to a white heat †. The fact was afterwards established by Mr Wedgwood. Air was passed through an earthen tube, in a state

* Chemical Essays, p. 33.

† Philosophical Transactions, vol. lxvi, p. 504.

of ignition, and was conducted into a globular vessel, from which, by an opening in the top, it was allowed to escape; while, by another opening in the side, closed by a piece of glass, the eye could be directed into the inside of the globe. On looking into it, the air which had passed through the ignited tube was not luminous; but if a solid body, as a piece of gold, was suspended in it, this became luminous*. This is probably owing to the tenuity of æriform fluids, whence they present too few points in a given space to project a quantity of light sufficient to excite vision, though their particles may individually be in a state of ignition.

The phenomena of ignition are produced, not only by heat, but likewise by percussion and attrition. When a piece of steel is struck against a flint, small particles of the metal are detached, which are at a red heat. Or if hard minerals be made to rub strongly against each other, they give out light. Thus, by applying quartz or agate to the circumference of a wheel of fine grit, revolving at a moderate rate, Mr Wedgwood observed, that the substance applied became brightly red, at the touching part; if the wheel revolved at a quicker rate, the part in contact emitted a pure white light; and in both cases, glowing sparks were emitted, some of which were not extinguished before they had passed a foot through the air. They exploded gunpowder and inflammable air, and burnt the skin, a sufficient proof that they were not merely luminous or phosphorescent, but ignited, or at a red heat. In the same mode, glass and porcelain were raised to a red heat. These appearances from attrition are probably to be ascribed to the heat which is excited rising sufficiently high to extricate their light, as the same bodies become luminous when directly heated, and as the same appearances are not produced in substances which are soft, these not having their temperature raised by attrition †.

* Philosophical Transactions, 1792.

† Ibid. p. 39.

Ignition is sometimes produced by the temperature being raised sufficiently high by chemical action to excite it, as in the affusion of concentrated acids, such as the sulphuric on dry earths, as magnesia, or even in the slaking of lime highly calcined.

On the cause of ignition different opinions have been entertained. Those who suppose light and caloric to be modifications of the same substance, and to be mutually convertible, regard the phenomena of ignition as arising from the conversion of caloric into light,—an hypothesis, as I shall afterwards have to shew, which is improbable. Others have supposed, that the light extricated is a constituent principle of the ignited body, and is expelled by the repulsive agency of caloric. The objection to this is, that, admitting light to exist in incombustible bodies, it must be contained in them in limited quantity, and therefore its emission in ignition should diminish, and at length cease. Perhaps it is necessary to separate the causes by which ignition is effected, in the consideration of its theory. When it is excited by communication with a hot body, it probably receives from that body the light as well as the caloric. Thus, if placed amid burning fuel, both light and caloric are evolved from the combustion; the ignited body is penetrated with caloric, which it gives out; it is equally exposed to the light from the combustion, may receive it, and throw it off from its surface: and even when removed from the fuel, it will continue to emit both. The experiment of Wedgwood, in which ignition was excited by applying to the body a stream of air highly heated, but not luminous, may be supposed adverse to this explanation; but it is easily reconciled with it, as the heated air, though not luminous from the cause already stated, its great tenuity, may still have conveyed light. With regard to the production of ignition by attrition, the same difficulty will be found in accounting for the evolution of caloric as for the evolution of light. It is

not proved that ignition can in this case be kept up for an indefinite time, as it can by communication with matter in a state of combustion ; and the light which does appear may be the light contained in the body, expelled by the high temperature which the friction or percussion excites. At the same time, it is to be remarked, that with regard to the excitation of all these subtle principles or forces, caloric, light and electricity, there are difficulties of which the present state of our knowledge probably does not enable us to give a satisfactory solution.

The effects of caloric in causing chemical combinations and decompositions have been explained under the doctrines of Chemical Attraction ; they cannot indeed be considered as a primary result of its operation, but as arising from the expansion it occasions ; which, by weakening the attraction of cohesion, in some cases favours combination ; and in others, by increasing elasticity, counteracts it, and acting unequally on the elements of a compound, separates them from each other, or gives rise to decomposition.

SECT. III.—*Of the Communication and Diffusion of Caloric.*

CALORIC has an invariable tendency to diffuse itself over matter, so as to establish uniformity of temperature. Hence when bodies at different temperatures are placed in contact, either directly, or by the medium of some other substance, those which are at a higher temperature part with caloric to those which are at a lower; and this reciprocal emission and absorption continue until a common temperature is formed. It is impossible to preserve a body highly heated in that state; however we may place it, it will, when removed from the source of caloric, begin to give out the heat it had received, and will continue to do so until it is at the same temperature with those around it: Or if a body has been rendered intensely cold, it is equally impossible to preserve it so; it will imbibe caloric from the surrounding matter, until it has attained an equality of temperature.

This tendency of caloric to an equilibrium of temperature seems in a great measure to arise from its repulsive power. When a hot body is placed among others that are colder, the excess of heat in the former leaves it, not so much from any attraction exerted to it by the other bodies, as from the tendency of caloric to exist every where in what has been termed an equality of tension or repulsion. The proof of this is, that a body at a high temperature, placed in the Torricellian vacuum, suffers reduction of temperature, the caloric emanating until it arrive at an equilibrium with that in the surrounding bodies. Yet the distribution of caloric cannot be ascribed entirely to this cause; for were it retained in bodies only by the resistance opposed to its escape, from the equality of tension in which it exists at the same time in the surrounding matter, it ought to escape from, or enter different bo-

dies, when at the same temperature, and exposed in the same medium, with equal celerity. This is not the case. Different bodies at the same temperature are cooled with different degrees of celerity, and different *media* accelerate heating and cooling in bodies placed in them in very different degrees. A body at a high temperature will be cooled more quickly if plunged in water than if suspended in atmospheric air, and still more so in quicksilver than in water : or if at a low temperature, it will be heated faster in the quicksilver than in the water, and in the water than in the atmospheric air, though the temperatures of all these may have been previously the same. It will also cool more quickly when surrounded with any material medium, than when it is placed in a vacuum.

From an attentive examination of these phenomena, it has been discovered, that this propagation of caloric over matter takes place in two modes. Of the caloric emanated from a body at a high temperature, part appears to be projected from its surface in right lines with great velocity ; and another portion is communicated more slowly to the matter which is in contact with it, is conducted through that matter from one particle to another, and is given in like manner from it to other bodies, with a celerity greater or less, but always comparatively moderate. The former is little if at all dependent on the nature of the surrounding medium, at least if it be an elastic one, while the latter is materially influenced by it. The distribution of caloric may be considered under these two modes— of Radiation and of Slow Communication.

1. OF THE SLOW COMMUNICATION OF CALORIC.

CALORIC communicated to a mass of matter diffuses itself through it equally, so as to establish ultimately uniformity of temperature. And in a solid body this diffusion takes place by the direct communication from one portion to another. The effect depends on the tendency of this power to exist in a state of equilibrium, and hence it is immediately dependent on inequality of temperature. The part of the solid receiving heat has its temperature raised; in consequence of this, it communicates a portion of its excess to the contiguous part; this from the same cause yields a portion to the next, and thus losing part of its excess, it again receives a portion from the first. In this manner each contiguous part receives heat from the former in a decreasing series, and it is only if the heat is confined at the surface, that a common temperature is ultimately established. If it is allowed to escape freely, no common temperature will be formed; and if the communication preserve a due proportion to the escape, the temperature at the extremity may never even rise.

This diffusion of caloric through a solid body is best illustrated by observing the transmission of temperature through a rod having thermometers placed at regular intervals, and receiving heat at one extremity. The experiment was made with accuracy by Biot. He employed a bar of iron 22 decimetres (about 7 feet) in length, and 3 centimetres (about $\frac{1}{2}$ inch) in breadth, bent at one extremity, so that this could be immersed in a medium affording a constant source of heat, holes were placed at equal distances in the bar, in which the bulbs of thermo-

meters were inserted, immersed in quicksilver; and heat was applied to the bent extremity by immersion in quicksilver kept at a constant elevated temperature. Finding in his first trials, that the heat was diffused much less rapidly than he had expected, he placed the thermometers, by means of proper cavities, at the distance of one decimetre from each other, commencing at that end of the bar to which the heat was applied. The quicksilver in which this was immersed was kept at the temperature of 82 of Reaumur (216 of Fahrenheit,) for five hours. At the end of four hours the thermometers had become stationary; they were allowed to continue so for an hour, and then the temperatures were taken. The temperature of the first was 23.5 (Reaumur,) of the second 14, the third 9, the fourth 5.75, the fifth 3.75, the sixth 1.75, the seventh 1, this last being distant from the surface of the heated quicksilver 10 decimetres. The thermometer beyond it was never sensibly affected, and hence more than half the rod remained without any rise of temperature; nor could the extremity of it be possibly affected, as the heat necessary for that purpose at the commencement would have been more than sufficient to melt the iron *.

These results give the temperatures in geometrical progression nearly, taking the distances in arithmetical progression, any deviation from this being inconsiderable, and not greater than what may be allowed for errors in the experiment.

The diffusion of heat through a body will be equally produced in another mode,—that of reducing the temperature at one extremity. The portion cooled receives, in consequence of this, caloric from that which is contiguous to it; this losing a portion of its heat, receives for the same

* Journal des Mines, t. xvii, p. 203.

reason a portion from the next, in consequence of which, its temperature still remains superior to that of the first, and it thus yields a portion of caloric to it, while by doing so it is equally disposed to receive caloric from the other. A series is thus established, each part yielding and receiving caloric with a decreasing temperature through the whole.

If the escape of heat is prevented, then a state of equilibrium will at length be attained. The part from which the caloric does not escape, will still continue to receive caloric from the contiguous portion, as long as the temperature of the latter is superior to that of the other; the communication will cease only when the temperature is the same, and from the same cause this will be the case through every part of the mass, and a common temperature must in consequence be established *.

In this diffusion of caloric, the higher the heat communicated, or the greater the cold applied, the diffusion will be more rapid, as the difference of temperature on which it depends will be greater.

In the communication of heat from one body to another, the same law prevails as in its distribution from one portion of a body to another portion,—that is, the communication depends entirely on inequality of temperature, and will continue until a common temperature is formed. But in different bodies the celerity of communication and distribution is very various. Some bodies receive caloric quickly from others, convey it quickly through their mass, and yield it quickly to others, while other bodies do so much more slowly. The property in bodies on which this depends is named their conducting

* These laws with regard to the diffusion of heat, have been well illustrated by Mr Playfair. (Edinburgh Philosophical Transactions, vol. vi, p. 355.)

power with regard to heat : those which receive, convey, and communicate it quickly, being considered better conductors than those in which these changes take place with less celerity.

The difference in this respect is very apparent in different bodies. If a rod of iron and a rod of glass be held in the hand, the extremity of each being put into a common fire, the heat will pass so quickly through the iron rod, that the hand will soon be unable to retain it ; while the glass rod may be held for any length of time. Or an earthen vessel, containing water, nearly boiling hot, may be easily held in the hand, while a metallic vessel, containing water, at the same temperature, can scarcely be touched.

In general, dense bodies are the best conductors of caloric ; and those which are more rare and spongy, conduct it imperfectly. The metals, which are the substances of greatest density, are those which transmit it most rapidly ; earthy substances conduct it more slowly ; wood is a very imperfect conductor, and the spongy materials which form the covering of animals, hair, fur, feathers, &c. are inferior to every other solid matter in their conducting power. Even the same kind of matter, in its different states of aggregation, differs in this property : an iron bar, or an iron plate, is a better conductor than iron-filings, and saw-dust is a worse conductor than wood.

Richman made some experiments on the conducting power of various metals, with the view of discovering whether any relation could be traced between it and some other properties of bodies, with which it had been supposed to be connected. He inclosed the bulb of a thermometer in similar hollow balls of the metals, which were plunged into boiling water, until the thermometer in each rose to the same point. They were then removed, and exposed to the atmosphere, and the time which elapsed while the inclosed thermometer cooled a certain number

of degrees, was marked : the relative conducting power was ascertained by the times of cooling. Brass and copper appeared to have the greatest power of retaining caloric, and were equal to each other ; next to these was iron ; then tin ; and lead appeared, to use Richman's phrase, to have the least power of retaining heat, the decrements of temperature in all of them being in the following proportions : brass 10 ; copper 10 ; iron 11 ; tin 17 ; lead 25. With regard to the general object of his experiments, he inferred, that the decrements and increments of temperature in these bodies are not in the inverse ratio of their density, of their cohesion, or of their hardness, or in any compound ratio of these *, and, of course, can be discovered only by experiment.

Ingenhouz employed a different mode of experiment. Selecting wires of different metals, of the same diameter, they were plunged into the same quantity of melted wax, to the depth of eight inches ; in withdrawing them, each was thus covered with a coating of wax. When cold, they were plunged into heated oil, to the depth of about two inches. On withdrawing them, the length of wax-coating melted shewed the extent to which the heat had penetrated the metal, and, by this, their relative conducting powers. Silver he found to be the best conductor, gold held the second place, tin and copper were next, being nearly equal ; next to these were platina, steel, iron, and lead, which did not differ much ; lead, however, was evidently the worst conductor †. It appears from these results, that although density is favourable to the transmission of caloric through bodies, the conducting power is not precisely as the density ; lead and platina, which are heavier than copper or tin, being less perfect conductors. The experiments of Ingenhouz, though they cannot be regarded as perfectly

* Comment. Petropol. tom. iv, p. 241.

† Journal de Physique, tom. xxxiv, p. 68.

accurate, are superior to Richman's, as, in the latter, the discharge of caloric by radiation is not separated from that by communication.

No accurate experiments have been made on mineral substances as to their conducting powers. Meyer made some experiments on the conducting powers of different woods, by placing the bulb of a thermometer in perforated balls of the same diameter, filling up the cavity with dust of the same kind of wood, and exposing the balls to heat, until the thermometers were heated to the same point; then allowing them to cool suspended in the atmosphere. The conducting power of elm wood estimated in this way, from the time of cooling, being stated at 1000, that of oak was 1003, of pine 1152, of alder 1182, of fir 1189, of beech 987, of ash 946, and of ebony 667 *.

In all these experiments, however, there are sources of fallacy, although the results may in a general sense be just. The communication or abstraction of caloric by radiation, has not been sufficiently distinguished from that by slow communication; and due attention has not always been paid to the quantities of caloric requisite to produce changes of temperature in different bodies. This last circumstance was remarked by Humboldt, who has given a table of the conducting powers of a number of bodies, (*Journal de Physique*, t. xliii, p. 306 :) but it appears to be so inaccurate that no confidence can be placed in it.

Rumford, with the view of discovering the relative degrees of warmth of articles of clothing, made experiments on the substances of which they are composed. His method was, to suspend a thermometer in a cylindrical glass tube, the extremity of which had been blown to a globe, $1\frac{6}{10}$ inch in diameter, the bulb of the thermometer being in the centre of the globe. It was then surrounded with

* *Annales de Chimie*, tom. xxx, p. 39.

the substance; and the instrument was heated in boiling water, and afterwards being plunged into a mixture of pounded ice and water, the times of cooling were observed*. The following are the results; the number of seconds being marked, during which the thermometer cooled from 70° to 10° , of the scale of Reaumur. Air, 576''; raw silk, 1284''; wool, 1118''; cotton, 1046''; fine lint, 1032''; beaver's fur, 1296''; hare's fur, 1315''; eider down, 1305''. The relative conducting powers, being inversely as the times of cooling, hare's fur and eider down are the worst conductors, lint the best. The experiment was repeated with fine powder of charcoal, lamp black, and pure dry wood ashes. The times of cooling of these, through the same extent of the thermometrical scale, marked in seconds, was for the charcoal 937'', the lamp-black 1171'', and the wood-ashes 927''.

The relative conducting powers of these substances appeared to depend on the quantities of air inclosed in their interstices, and the force of attraction by which this air is retained or confined. If their imperfect conducting power depended on the difficulty with which caloric passes through their solid matter, the relative degree of that power would be as the quantity of that matter. The reverse, however, is the case. It was found, that by varying the arrangement of the same quantity of matter, the conducting power was varied. The thermometer being surrounded with 16 grains of raw silk, the times of cooling from 70° to 10° of Reaumur amounted to 1284''; with ravellings of taffety 16 grains, 1169''; and with sewing silk cut 16 grains, 917''. Here it was obvious, that the more dense the same matter was, or the less air it contained, diffused through its interstices, the caloric passed with more celerity. It is evident also, that the air remaining in the globe, in these

* Essays by Count Rumford, vol. ii, p. 428.

experiments, if the motion of its parts had not been impeded, would have been sufficient of itself to have carried off the caloric more quickly than it actually was; for air in motion conveys changes of temperature with celerity, and hence the interposition of the fibrous matter must have acted principally by retarding the motions of the included air, partly also probably by retarding the discharging of heat by radiation. The former effect will be in a great measure proportionable to their sponginess, and to the force of attraction with which the air is retained in their interstices. That such an attraction exists, is proved by the force with which they retain the air, which adheres to them even when immersed in water, or exposed under the exhausted receiver of the air-pump. It is to this cause principally, that the property which all porous bodies, such as furs, feathers, wool and down, have of retarding the passage of caloric, is owing; and hence they form the warmest articles of clothing. On this also depends the imperfect conducting power of snow, which, in consequence of it, serves the important purpose of protecting vegetables from intense cold.

When we wish to confine caloric, we avail ourselves of this difference in conducting power, and employ substances which are imperfect conductors. Thus furnaces are coated with a mixture of clay and sand, to prevent the dissipation of heat. To exclude caloric, or to prevent it from being communicated to a body from the surrounding medium, the same method must be employed,—surrounding the body with an imperfect conducting substance. On this principle ice-houses are constructed.

From the difference among bodies, in their power of conducting caloric, arise the differences in the sensations of heat and cold, which they excite when applied to our organs, though the thermometer shews that they are at the same temperature. The sensation of cold is produced by whatever abstracts caloric from the part to which it has

been applied ; and of two bodies at the same temperature, the one, which is the best conductor of caloric, will abstract it most rapidly, and therefore occasion a more intense sensation of cold. The sensation of heat is produced, when caloric is communicated to the sentient part ; that body, which is the best conductor, will communicate a larger quantity in a given time, and therefore, when applied hot, will excite a greater sensation of heat than another will do at the same temperature, which is a less perfect conductor. Hence, a piece of metal, at a low temperature, feels colder than a piece of wood, though their temperatures are proved to be the same by the thermometer ; and, on the contrary, it will at a high temperature feel hotter than the other.

The preceding observations are applicable only to the conducting power of substances in the solid form. With regard to liquids, the mode in which caloric is distributed through their substance, so as to establish uniformity of temperature, is in part different. Besides, the communication of caloric from the proper conducting power, changes in the temperature of a liquid are influenced by the motions of its parts. When heated it is expanded, and of course has its specific gravity diminished ; from its mobility, the heated portion rises to the surface of the mass ; a new portion of fluid comes in contact with the part from which caloric is communicated, is heated, and rises in its turn ; and thus the whole portion of fluid is brought successively into contact with that part ; and these motions must continue, as long as caloric continues to be communicated. In both these modes, caloric was conceived to be diffused through any mass of liquid, so as to raise its temperature. It was also supposed, that fluids differ in their conducting power, and experiments were instituted to ascertain these differences.

In opposition to this opinion, Count Rumford advanced

the doctrine, that caloric is diffused over any mass of fluid in one of these modes only, — by the movement and successive application of the fluid to the surface from which the caloric is communicated ; and that the portion heated, imparts none of its caloric to the rest of the mass through which it ascends.

He was led to form this opinion, from several observations on the slowness with which caloric is distributed through a fluid, when the motions of its parts are impeded ; and on the rapid movements which do take place in it, when it is suffering change of temperature. But allowing to these observations all the importance which Rumford assigned to them, they only prove what was never doubted, that a liquid must have its temperature raised in part by the different portions of it coming successively into contact with the surface through which caloric is communicated ; without proving, that the liquid is heated solely in this mode.

He adduced some other facts to establish this, and to prove, that in fluids no communication of caloric from particle to particle takes place. His experiments on this subject will be found in his *Essays* : all of them are inconclusive. In one series, it was shewn, that when the motions of a fluid are impeded, by dissolving in it any substance which renders it viscid, or by intermixing with it any imperfect conducting solid, the transmission of caloric through it is rendered very slow, an effect which might well happen from the obstacle to the motions of the liquid, though the communication of caloric still also took place. In another series of experiments, it is attempted to be proved, that heat is not conveyed downwards through a fluid ; and had this been established, the opinion would have been demonstrated, since a liquid, if capable of communicating caloric from particle to particle, ought to convey it in every direction. But these experiments are equally defective. It was shewn, indeed, that caloric is conveyed downwards very slowly ; that water, for example, may be made to boil

in the upper part of a tube, without that at the bottom being much heated; that it may even be made to boil within one-fourth of an inch of ice without immediately melting it; and that ice fixed at the bottom of a cylindrical vessel, with warm water above it, is melted more than eighty times slower than when it floats on the surface of the water. But in all of them, either the arrangements are obviously such as to diminish any effect from the conducting power of the fluid, or so many assumptions are made in shewing that their results are favourable to the non-conducting power of liquids, that they are altogether unsatisfactory.

In opposition to the opinion, that fluids are non-conductors of caloric, a number of experiments have been made, by which its fallacy is demonstrated.

At an early period, Dr Hope made some experiments on this subject. He found, that on applying heat to the surface of water in a vessel 11 inches in diameter, causing a stream of water to circulate on the outer side of the vessel at the same height as the surface of the liquid within to obviate the conducting power of its sides, caloric was conveyed downwards, as was discovered by the indications given by a thermometer beneath; and that, on mixing portions of hot and cold water, and allowing the mixture, after agitation, to remain at rest, no separation took place;—results both of them inconsistent with Rumford's opinion*. Dr Thomson likewise found that caloric was conveyed downwards through water and quicksilver when heat was applied to their surface†. Experiments with a similar result were made by Mr Nicolson‡, and Mr Dalton§. I had also found that a liquid was heated downwards

* Transactions of the Royal Society of Edin. vol. v, p. 394.

† Nicolson's Journal, 4to, vol. iv, p. 529.

‡ Ibid. vol. v, p. 197.

§ Manchester Memoirs, vol. v, p. 373.

when a hot body was placed at its upper surface, even when the containing vessel was surrounded with water to obviate its conducting power.

Whatever precaution, however, is taken to obviate the fallacy from this last circumstance, we can scarcely be certain that it is entirely removed. Thus, if we take the most effectual mode, that of surrounding the jar externally with water, although part of the caloric conveyed downwards by the sides of the vessel will be abstracted by this external water, yet another part must be given to the liquid within the vessel, and may accumulate until the portion thus heated reach the thermometer; nor is it possible to determine with accuracy what proportions of the caloric which the vessel conveys are given off at its external, and at its internal surface, so as to make due allowance for its effect in the experiment. Any other precaution, too, which we take to guard against this source of inaccuracy, such as employing a wide vessel, or interposing a great depth of fluid between the thermometer and the body communicating caloric, defeats the purpose of the experiment, since such precautions, while they lessen the effect from the communication of caloric by the vessel, lessen equally the effect which would result from a conducting power in the fluid, if it do possess it; and therefore it must remain uncertain to what the diminished effect is to be ascribed.

It occurred to me, that this source of uncertainty might be obviated by a simple contrivance,—employing a vessel of ice in which a fluid at 32° should be placed. Ice cannot have its temperature raised above 32° of Fahrenheit; for if heat be communicated to it, it is spent merely in melting it. Hence it cannot communicate any temperature above that point, and therefore, if a fluid contained in a vessel of ice be heated downwards, by a hot body being applied to its surface, we may conclude with certainty that the caloric has been conveyed by the conduct-

ing power of the fluid. In a hollow cylinder of ice, a thermometer was placed horizontally, at the depth of one inch, its bulb being in the axis of the cylinder, and the part of the stem to which the scale was attached entirely without. As water could not be employed at the temperature at which it is requisite to make the experiment, on account of the property it possesses of becoming more dense in the rise of its temperature from 32° to 40° , oil was used. A quantity of almond oil, at 32° , was poured into the ice cylinder, so as cover the bulb of the thermometer $\frac{1}{4}$ inch. A flat-bottomed iron cup was suspended, so as to touch the surface of the oil, and two ounces of boiling water were poured into it. In a minute and a half, the thermometer had risen from 32° to $32\frac{3}{4}^{\circ}$; in 3 minutes, to $34\frac{1}{2}^{\circ}$; in 5 minutes, to $36\frac{1}{4}^{\circ}$; in 7 minutes, to $37\frac{1}{2}^{\circ}$, when it became stationary, and soon began to fall. When more oil was interposed between the bottom of the cup and the bulb of the thermometer, the rise was less; but even when its depth was three quarters of an inch, the rise amounted to $1\frac{1}{2}$ degree. With mercury the same results were obtained, the thermometer rising only with much more rapidity, from the mercury being a better conductor than the oil *.

These experiments I would regard as decisive, in establishing the conducting power of fluids. The source of error from the sides of the vessel is entirely obviated; no currents could be formed, by which the rise of the thermometer could be occasioned, nor is there any mode in which that effect could have been produced, but by the fluid conducting the caloric from particle to particle.

Still there is reason to believe that fluids are very imperfect conductors of caloric, and that the distribution of caloric through them is in a great measure by the circulation of their parts; for we find, that when this is impeded or prevented, the communication is extremely slow.

* Nicolson's Journal, 8vo, vol. i, p. 241.

According to Rumford, ice is melted eighty times slower when at the bottom of a column of water, than when floating on its surface; and, if we exclude the partial circulation, which even in the former case takes place, from the increased density of the water, as it is heated from 32° to 40° , and from the influence of the containing vessel, the difference must be more considerable, and amply demonstrates the imperfect conducting power of the fluid.

It is difficult to ascertain the relative conducting powers of different fluids, because it is difficult to determine what proportion their real conducting power bears to that mobility by which circulation of their mass takes place, when they are subjected to a heating or cooling cause, and by which uniformity of temperature through them is chiefly established. Mercury, from the facility with which it receives changes of temperature, is evidently superior in conducting power. Count Rumford, in some early experiments on the conducting powers of bodies, found, that when the thermometer was surrounded with quicksilver, it required to raise it to a certain extent of temperature, immersion in boiling water for $36\frac{2}{3}$ seconds, while, when surrounded with water, the time requisite for raising it the same extent was $1'57''$, or 117 seconds*. Hence the conducting power of the quicksilver is to that of water, as $36\frac{2}{3}$ to 117 inversely, or directly as 1000 to 313. But though this may approach to the real difference between them in conducting power, it may not express it with perfect accuracy, as the result must be dependent also on the greater or less mobility of the fluid, and on the degree of expansion which each suffers from the communication of a given quantity of caloric, by which, as it is more considerable, the circulation arising from the difference of specific gravity, in the hot and cold portions, will be rendered more rapid. Allowing, however, for these circumstances,

* Essays, vol. ii, p. 425.

we can in some cases discover the predominance of the real conducting power, though we may be unable to ascertain its extent with perfect accuracy. Thus quicksilver suffers less expansion from a given change of temperature than alcohol does, and therefore, while receiving caloric, the internal circulation of its parts must be less rapid, as there will be less difference of specific gravity between the portion heated and that which is not; yet it takes the temperature of the surrounding medium more quickly than alcohol, as is evident from the greater delicacy of the mercurial than the spirit thermometer. This proves a superiority in its proper conducting power.

My friend Dr Traill, who added some arguments to those before stated against Count Rumford's conclusions as to the non-conducting power of fluids, endeavoured to ascertain the conducting powers of different liquids, by finding the times requisite to raise a mercurial thermometer, placed in the liquid submitted to trial, 3 degrees of Fahrenheit, in consequence of the transmission of caloric downwards, from the extremity of a cylinder of iron, one inch in diameter, heated to 212° , and suspended in the liquid so as to be distant from the bulb of the thermometer 0.5 inch. The results are given in the following table *, shewing the times in minutes and seconds.

Mercury,	-	-	-	0' 15 ^h
Saturated Solution of Sulphate of Soda,	-	-	-	6' 30''
Water,	-	-	-	7' 5''
Proof Spirit,	-	-	-	8' nearly.
Solution of Sulphate of Iron, 1 of salt to 5 of water,	-	-	-	8'
Water of Potassa,	-	-	-	8' 15''
Milk of a Cow,	-	-	-	8' 25''
Saturated Solution of Sulphate of Alumine,	-	-	-	9' 40''
Transparent Olive Oil,	-	-	-	9' 50''
Alkohol, Lond. Pharm.	-	-	-	10' 45''

* Nicolson's Journal, vol. xii, p. 137.

From the manner of executing these experiments, no important influence can be ascribed to any circumstance, independent of the proper conducting power of the liquids, as little effect could be produced by any differences which might exist in expansibility or mobility; nor can the results be accounted for on any differences of this kind.—They must, therefore, be regarded as nearly indicating the different conducting powers.

Rumford advanced the same opinion with regard to airs as with regard to non-elastic fluids,—that they are non-conductors of caloric, and that caloric is distributed through them entirely from the motion of their parts. The experiments by which he endeavoured to support this, are similar to those from which the non-conducting power of liquids was inferred; and, from the greater difficulties which attend the execution of them, they are still less conclusive. The same conclusion is probably to be drawn as to the general question. The reason why a liquid conducts caloric so slowly, is apparently, that, from the mobility of its parts, as soon as a particle is heated it recedes from the others, and does not communicate the caloric it had received. The same cause, it may be inferred, must operate in the aëriform fluids, and render them imperfect conductors, though there is little probability in the conclusion, that they are altogether incapable of conducting caloric.

Berthollet, however, has advanced the opinion, for which there seems to be some reason, that aëriform fluids, so far from being imperfect conductors of caloric, conduct it with rapidity. The familiar example of the celerity with which an air thermometer indicates change of temperature, he regards as a proof of this; and also the fact, that aërostats have sometimes experienced a sudden dilatation of the air in their ballóon, from the appearance of the sun. He remarks, that the particles of the contained air cannot be supposed to take the increased temperature which the ex-

pansion indicates, by being brought individually, and of course successively, to the covering of the balloon ; and still more, that the lower particles, which are contiguous to that portion of the covering which does not receive the solar beams, cannot be heated in this manner. Hence he concludes, that these phenomena indicate, that the elastic fluids, far from being imperfect conductors, receive the temperature of others very quickly *. The result which Rumford's experiments appear to establish, that air, when confined, impedes the communication of caloric, he supposes to be owing to the state of compression in which it exists, by which its dilatation is prevented, and this opposes an obstacle to the caloric diffusing itself.

There appears even to be a difference in the celerity with which different bodies in the aerial form conduct caloric. An example of this is in air which is dry, compared with air loaded with moisture. In some early experiments by Rumford, a thermometer surrounded with humid air was more rapidly heated when exposed to a source of caloric than when surrounded with air perfectly dry, the time required to raise it in dry air from 32° to 212° , by plunging the vessel containing it into boiling water, being 8 minutes 9 seconds ; while, in moist air, it required only 1 minute 51 seconds, a difference as 330 to 80 †. There is, indeed, an error in this experiment, from the circumstance, that to render the air humid, the sides of the vessel were wetted with water, which, when converted into vapour, would condense in part on the cold bulb of the thermometer, and by the latent heat it would give out, would contribute to raise its temperature ; and accordingly, in the reverse mode of making the experiment, or observing the time the thermometer takes to cool in dry and

* Chemical Statics, vol. i, p. 465.

† Essays, vol. ii, p. 417.

humid air, the difference does not appear so considerable. Still it is apparent. And some difference in conducting power is even obvious, in the effects of air in these states on our sensations ; damp air when at a moderate or rather low temperature, feeling colder than air at the same temperature which is perfectly dry. Mr Leslie observed with more precision, that the times of cooling of bodies are very different in the different elastic fluids ; in hydrogen gas it takes place much more rapidly than in atmospheric air ; and in carbonic acid gas it takes place very slowly. These results have been confirmed in a repetition of the experiment by Mr Dalton. The refrigeration depends on the radiation of caloric, as well as on the communication of it to the surrounding matter ; but these differences, Mr Leslie found reason to conclude, arose principally from the different conducting powers of the different elastic fluids.

In concluding this subject, it may be observed, that it is principally by the agency of fluids, elastic and non-elastic, that the distribution of caloric over the globe is regulated, and great inequalities of temperature guarded against ; and that this agency is exerted chiefly by the circulation of which their mobility renders them susceptible.

Thus the atmosphere with which the earth is surrounded, serves the important purpose of moderating the extremes of temperature in every climate. When the earth is heated by the sun's rays, the stratum of air reposing on it receives part of its caloric, is rarefied, and ascends. At the same time, from a law which attends the rarefaction of elastic fluids, that they become capable of containing a larger quantity of caloric at a given temperature as they become more rare, this heated air, though its temperature falls as it ascends, retains the greater part of its heat ; its place at the surface is supplied by colder air pressing in from every side ; and, by this constant succession, the heat is moderated that would otherwise become intense. The heated air is, by the pressure of the constant ascending

portions, forced towards a colder climate : as it descends, to supply the equilibrium, it gives out the heat it had received, and this serves to moderate the extremes of cold. There thus flow a current from the poles towards the equator, at the surface of the earth, and another superior current from the equator to the poles ; and though the directions of these are variously changed, by inequalities of the earth's surface, they can never be interrupted, but produced by general causes must always operate, and preserve more uniform the temperature of the globe.

Water is not less useful in this respect in the economy of nature. When a current of cold air passes over the surface of a large collection of water, it receives from it a quantity of caloric ; the specific gravity of the water is increased, and the cooled portion sinks. Its descent forces up a portion of warmer water to the surface, which again communicates a quantity of caloric to the air passing over it ; and this process may be continued for a considerable time, proportioned to the depth of the water : If this is not very considerable, the whole is at length cooled to 40° , below which, the specific gravity not increasing, the circulation ceases, and the surface is at length so far cooled as to be covered with ice. If the depth is much greater, the application of the cold air may be continued longer without this result ; and in this, and other countries not intensely cold, it often happens that deep lakes are not frozen in the course of the winter. The depth of the ocean being greater, and the body of water larger, while, from its saline impregnation, its points, both of freezing and maximum density, are lowered, it resists freezing still more effectually, and is scarcely frozen indeed except in latitudes where the most intense cold prevails.

The quantity of caloric thus communicated by water is exceedingly great. The heat, Count Rumford remarks, " given off to the air by each superficial foot of water, in cooling *one* degree, is sufficient to heat an incumbent stra-

tum of air 44 times as thick as the depth of the water. 10 degrees. Hence we see how very powerfully the water of the ocean, which is never frozen over except in very high latitudes, must contribute to warm the cold air which flows in from the polar regions." From this cause currents must exist in the ocean similar to those formed in the atmosphere. The water which, in the colder regions, is cooled at the surface, descends, and spreading on the bottom of the sea, flows towards the equator, which must produce a current at the surface in an opposite direction; and thus the ocean may be useful in moderating the excessive heats of the torrid zone, as well as in obviating the intense colds of the polar climates.

II. OF THE RADIATION OF CALORIC.

I HAVE remarked, in the beginning of the present section, that caloric is diffused over matter, not only by slow communication, but that, from a body at a high temperature, it is likewise projected in right lines, moving with great velocity, and obeying the same laws of motion as the rays of light. This constitutes its Radiation, the subject I have now to consider.

This property of caloric had not escaped observation even at an early period. In the Memoirs of the Academy of Sciences for 1682, an experiment of Mariotte is stated, in which it is said, that "the heat of a fire, reflected by a burning mirror, is sensible in its focus; but if a glass be interposed between the mirror and the focus, the heat is no longer sensible." Lambert made a similar experiment, and shewed more clearly, that the heat produced is not owing to the agency of light. Finding, that

from burning charcoal, placed properly between two concave mirrors, such a heat was produced, as to kindle a combustible body at the distance of 20 or 24 feet, to discover whether this arose from the light emitted, he collected in the focus of a large lens, the light of a clear burning fire, but found it to have scarcely any heat sensible to the hand *.

Scheele in his *Treatise on Air and Fire*, added several new and very important observations on this subject. He shewed, that this radiant heat, as he named it, passes through the air without heating it, and that any current in the atmosphere does not change its direction. If a pane of glass be interposed between the fire emitting it and the hand, it is arrested, and no sensation of heat is received, though the light from the fire is transmitted, and may be concentrated by a mirror, so as to form a bright image. A glass mirror, he observes, though it reflects the light of a fire, does not reflect the heat, but retains it, while a polished metallic surface reflects the radiant heat, as well as the light. A metallic mirror, therefore, opposed to a source of heat, may be held a long time without becoming warm. But he adds, that if it be blackened, it cannot be kept four minutes in the hand, opposed to a fire, without exciting too strong a heat to allow it to be held †. The general facts, for which we are indebted to Scheele, and which form the greater part of what has yet been discovered on this subject, are, That radiant caloric is reflected from metallic surfaces;—that it is not reflected or transmitted by a glass surface, but absorbed;—that when a metallic surface is blackened, it no longer reflects, but absorbs, and becomes therefore much sooner heated; that radiant caloric moves with velocity

* *Voyages dans les Alpes*, par Saussure, t. iv, p. 119.

† *Experiments on Air and Fire*, p. 67—71.

through air, undisturbed by any motion of the air, and without appearing to communicate to it any increase of temperature ; and that, when associated with light, it can be separated from it, so as to obtain the peculiar effects of each part from the other.

Saussure, in endeavouring to discover the cause of the cold that prevails on the summit of high mountains, was led to attend to the experiment of Lambert, and, in conjunction with Pictet, repeated and varied it. The apparatus they employed, represented Pl. IV, Fig. 39., consisted of two concave mirrors of tin, moderately polished, a foot in diameter, with a focus of $4\frac{1}{2}$ inches*. These were placed opposite to each other at the distance of 12 feet. In the focus of one was the bulb of a thermometer, in that of the other was put a ball of iron, 2 inches in diameter, raised to a red heat, and allowed to cool, until it was no longer luminous in the dark. The moment the ball was introduced, the thermometer in the opposite focus began to rise, and in six minutes it had risen from 4 degrees to $14\frac{1}{2}$ of Reaumur's scale, while another thermometer, suspended without the focus, but at the same distance from the heated ball, rose only from 4° to $6\frac{1}{2}^{\circ}$ †. The rationale of the experiment is sufficiently obvious. The heated body emits rays of caloric in right lines ; those of them which proceed towards the mirror, in the focus of which it is placed, are reflected and projected on the surface of the opposite mirror ; from it they are again reflected, and though at each surface some may be lost, yet

* In the Plate, the figures representing the different air thermometers and the differential thermometer are represented between the mirrors. These, in the description of the above experiment, are of course supposed to be removed. The ball on its standard represents the hot body in the focus of the one mirror B, the ball of the air thermometer is in the focus of the other A.

† Voyages dans les Alpes, t. iv, p. 120.

a sufficient number are united in the focus to produce an effect on the thermometer, while the thermometer without the focus receives only the few direct rays from the surface of the sphere, equal to its own surface to which it is opposed. The rise of temperature is of course greater, the hotter the ball is from which the caloric is discharged; and from a mass in a state of high ignition, it is sufficient to set fire to an inflammable body at the distance of several feet.

Pictet prosecuted these experiments. In substituting a burning candle instead of the heated ball, the thermometer rose from 4.6 degrees to 14° *.

In both experiments there was some ground for the suspicion, that light might give rise to much of the effect, for although the heated ball did not appear luminous even in the dark, this might be ascribed to the imperfection of vision; and as the temperature was so near to that of ignition, rays of light might still be discharged. To determine this point, Pictet repeated the experiment which had before been made, but with more accuracy,—that of interposing a plate of glass between the radiating body and the thermometer, which would afford a ready passage to any light present, while, if the rays were of the nature of caloric, these might be expected to be intercepted. When the burning candle had been placed in the focus, and had raised the thermometer in the opposite focus from 2 to 12 degrees, a plate of transparent glass was interposed, and in nine minutes the thermometer had descended to 5.7, that is more than one half. On removing the glass, it again rose. Even the effect which was produced while it was interposed, is probably not to be ascribed to the agency of light, but partly to the rays of caloric being imperfectly intercepted, and partly to the glass itself being

* *Essais de Physique*, p. 63.

heated by those which were arrested, and thus becoming a source of radiating caloric. He performed another experiment, in which the operation of light cannot be suspected. A glass matrass, capable of containing rather more than two ounces by measure, was filled with boiling water, and placed in the focus of one of the mirrors. The other was placed at the distance of 10 feet 6 inches, and in its focus was suspended a small mercurial thermometer, having Fahrenheit's scale. This in two minutes rose from 47° to $50\frac{1}{8}^{\circ}$; and when the matrass was removed, it began to fall. These experiments leave no room to doubt of the radiation of caloric, or they prove, that a calorific power is propagated in right lines from a mass of matter, the temperature of which is moderately raised.

It is known, that when bodies are blackened, they are more heated by the rays of light than when they are not so prepared. From the experiments of Scheele, in which he blackened the metallic mirror placed before a fire, and found it was more heated than when clean, it appeared to be the same with regard to radiant caloric; and this was farther ascertained by Pictet. When the bulb of the thermometer, which, by the caloric radiated from the matrass of boiling water, was raised from 47° to $50\frac{1}{8}^{\circ}$, was blackened, it rose, the experiment being in every other respect the same, from $51\frac{1}{8}^{\circ}$ to $55\frac{1}{4}^{\circ}$.

From Scheele's experiments might be collected, though with some obscurity, the effect of different kinds of matter at the same temperature, in radiating caloric. Experiments of a similar nature, though likewise obscure as to their rationale at that time, were made by Pictet, by interposing a glass mirror or plate, covered with amalgam on one side, between the hot body and the thermometer, and according as the glass or the metallic surface was opposed to the hot body, or according as either surface was

blackened, the calorific effect on the thermometer was different *.

In employing a concave glass mirror, scarcely any rise was indicated by a thermometer in its focus, when a heated metallic ball was opposed to it,—a very simple experiment, by which the different powers of glass and metal in reflecting caloric are also demonstrated.

Pictet, though he made the experiment, could not ascertain whether this radiating calorific matter suffered refraction. He endeavoured, but by a very rude experiment, to discover the velocity of its motion, placing two concave mirrors at the distance of 69 feet, with a skreen interposed, an air thermometer being placed in the focus of the one mirror, and a heated ball of iron being introduced into that of the other: on withdrawing the skreen the thermometer rose, nor was it possible to perceive an interval of time between its rise and the removal. The moment the skreen was dropped, the ascent of the thermometer ceased.

To these facts on radiant heat, Dr Herschel, a few years afterwards, added the important discovery, that rays of caloric exist in the solar beam, associated with visible light. He was led to this by finding, that when a ray of light is decomposed by the prism, the different coloured rays have different heating powers; the most refrangible of the visible rays, the violet, is least powerful in exciting heat, and the calorific power increases towards the other side of the spectrum, and is greatest in the red rays. This was ascertained by receiving the prismatic spectrum on a piece of pasteboard, in which was an opening of sufficient length to allow one of the prismatic colours to pass through. Very sensible thermometers were placed beneath, and by the rise they suffered, the heating powers of the different rays

* Essais, p. 72.

were compared *. In the red ray the rise was 7° , in the green ray $3\frac{1}{2}^{\circ}$, and in the violet ray only 2° .

But he further found, that entirely apart from visible light, beyond that side of the prismatic spectrum bounded by the red light, rays exist possessed of heating power, and this even to a greater extent than is possessed by the visible rays : the heating power is at its maximum half an inch beyond the visible light, and it can be traced to the extent of an inch and a half. This must be received as a proof of the existence of radiant caloric in the solar beam. The different heating powers of the different visible rays might be supposed to arise from differences in the rays themselves, as rays of light ; and did a certain degree of heat only exist beyond the red ray, inferior to that produced by the red ray itself, it might be ascribed to the diffused influence of this ray. But since the degree of heat is actually greater, the conclusion can scarcely be rejected, that it proves the presence of radiant caloric. The results established by Herschel were afterwards confirmed by the experiments of Englefield, and to a certain extent by those of Berard ; though in those of the latter the *maximum* of heating power appears to be within the boundary of the red ray, and to diminish beyond it. These are to be more fully stated under the history of Light.

From the separation of the calorific rays from the visible rays by transmission through a prism, it follows that the former as well as the latter are liable to refraction, since they are turned aside from their direct course. It appears even that a beam of radiant caloric must consist of rays of different refrangibility, for the calorific rays are dispersed over a space greater than that of the area of the prism, and greater even than that occupied by the visible rays of light. The range, therefore, of its refrangibility is even more extensive than that of the coloured rays.

* Philosophical Transactions for 1800, p. 257.

Herschel endeavoured to ascertain whether the radiant caloric projected from heated bodies is likewise refrangible. By placing a lens at a small distance from a burning candle, with a pasteboard skreen interposed, the direct rays from the candle, which passed through an aperture in the skreen, were refracted by the lens, and thrown on a thermometer in its focus, which was thus raised in three minutes $2\frac{1}{2}$ degrees *. A similar experiment was performed on the calorific rays issuing from a common fire, from a mass of red-hot iron, and likewise from iron heated, but not to ignition ; and the results equally proved, that these rays are subject to the laws of refraction. He also subjected to experiment the invisible calorific rays of the solar beam, and found that they were refracted to the focus of the lens †. It has been found by Berard, that both the solar calorific rays, and the calorific rays from hot bodies, are also susceptible of that modification by reflection, which constitutes polarization.

So far the radiant caloric which exists in the solar rays, and that emitted from bodies at a high temperature, agree in their properties. It follows, however, from Herschel's experiments, that a difference exists between them in one property, that of passing through transparent media, the latter being transmitted with much more difficulty than that which exists in solar light. He found, on exposing two thermometers of equal sensibility, the one covered with glass or some other transparent substance, the other remaining uncovered, first to the solar rays, and afterwards to the rays from a burning candle, that a greater proportion of the calorific rays in the latter were arrested by the glass than of the former ‡.

In these experiments, the radiant caloric was connected

* Philosophical Transactions, 1800, p. 272; Ibid. p. 309.

† Ibid. p. 317.

‡ Ibid. p. 446.

with light, which might influence its transmission through the glass. But when the invisible heating rays in the solar rays separated from the illuminating rays, and the invisible calorific rays emanated from a body heated, but not luminous, as from an iron stove, were operated on, the same general result was obtained *. There remains no doubt, therefore, as to the more difficult transmission of the radiant caloric from heated bodies through transparent media, compared with the radiant caloric which exists in the solar rays; and we can perceive, indeed, this difference from familiar facts. Water is scarcely *directly* heated by exposure to the solar rays, while its temperature is raised by being placed before a common fire; and the radiant heat of heated bodies is incapable of passing through a mass of water. When a plate of glass, too, is interposed between a heated body, placed in the focus of one mirror, and a thermometer in that of the other, the radiant caloric is nearly completely intercepted; while, when the solar rays are concentrated by a lens, a very intense heat is excited in its focus, a sufficient proof that the radiant caloric, or the greater part of it, existing in these rays, passes through the glass. Even a cloudy atmosphere, there is reason to believe, from natural phenomena, impedes greatly the discharge of radiant heat from the surface of the earth.

From subsequent experiments it appears, that the power of the calorific rays in passing through transparent *media* is considerably dependent on the temperature at which they are projected. There is some fallacy attending experiments to determine this, from the circumstance that the transparent body interposed between the source of heat and the thermometer is liable itself to become heated, and thus to radiate directly. And Mr Leslie had stated some experiments, proving, that when the interposed body

* Philosophical Transactions, 1803, p. 461, 485.

is not heated, as, for example, when a sheet of ice is employed as a skreen, no sensible transmission is indicated by any effect on the thermometer. But this mode of conducting the experiment is liable, as is afterwards to be stated, to some fallacy; and other experiments establish the reverse. Dr Maycock found, that a very sensible effect was produced on the common apparatus with the metallic mirrors, when a plate of glass was interposed between the hot body and the thermometer, employing as the source of heat either a burning candle or a flask of boiling water; and that the effect was not owing to the glass plate being heated and becoming a source of radiation, he proved, by finding that less effect was produced on the thermometer when a blackened glass skreen was interposed, than when clear glass was employed, though the former must have been considerably more heated than the latter; and also by the circumstance that when the heated body was removed, the glass plate being allowed to remain, the effect did not continue for a short time, as it ought to have done, if it depended entirely on the heat of the plate, but, on the contrary, the thermometer began immediately to fall *. Prevost obviated the fallacy in another mode, interposing moveable skreens of glass, which he renewed constantly so as to prevent their being heated, and still found that the radiant caloric passed through so as to affect the thermometer. And Delaroche, by interposing between the heated body and the thermometer, first a transparent skreen of glass, and secondly a skreen of blackened glass, and comparing the effect produced in each experiment, found how much was due to the heating of the skreen, and thus was enabled to determine any effect to be ascribed to the direct transmission through the glass. Making allowance for this, he obtained the same general result, that a portion of the calorific

* Nicolson's Journal, vol. xxvi, p. 75.

rays passes through the glass, and that this is greater as the temperature of the body projecting them is more highly elevated. If it is lower than 212° , the quantity transmitted is very inconsiderable; but as it rises above this, it is quickly increased. From this circumstance may be inferred the reason why the calorific rays in the solar beam penetrate transparent media with much more facility than those projected from heated bodies, as the former may be supposed to be thrown off at a higher temperature: and as the calorific rays acquire this power to a greater extent as the body approaches to ignition, at which it emits rays of light, this lends some probability to the conjecture, that the heating rays may become luminous by an increase of projectile force, and that radiant caloric may gradually by this progression pass into light.

Delaróche farther found, by interposing first one glass skreen, and then two skreens, and observing the difference in the effect, that the calorific rays which have passed through one skreen suffer a much smaller diminution of their intensity in passing through a second, than they did in passing through the first. This appears to prove, that the rays discharged simultaneously from a hot body are of different kinds, some passing with more facility through transparent media than others.

With regard to the law which is observed in the discharge of radiant heat in relation to temperature, he inferred from a number of experiments, that the quantity discharged is not merely proportional to the excess of the temperature of the hot body above the surrounding air, but that it increases in a much higher ratio*.

I have next to give an abstract of the important ex-

* Nicolson's Journal, vol. xxx, and xxxv. *Annals of Philosophy*, vol. ii.

periments of Mr Leslie, which discovered some other facts with regard to Radiant Heat, particularly the relation of different surfaces in emitting the calorific rays. He employed a single reflecting mirror of tinned iron, placed upright in a wooden frame. As the substance radiating caloric, he used small hollow cubes of tin, from three to ten inches, which were filled with hot water, and placed before the mirror at the distance of a few feet; by covering or preparing the sides of the cube in various ways, he could ascertain the effect of different kinds of matter on the radiation; and to ascertain the effect with more accuracy, at a temperature thus not very highly elevated, he employed the differential thermometer, the structure of which has been already described.

The tin vessel being filled with boiling water, and placed before the reflector, a few feet distant, and one of the balls of the thermometer being placed in the focus of the mirror, a rise of temperature is immediately indicated.

To examine the effect of different surfaces in radiating caloric, Mr Leslie painted one side of the vessel (a six inch cube), with lamp-black, coated another with writing-paper, covered the third with a pane of glass, and left the fourth uncovered. The vessel being filled with boiling water, and the black side being opposed to the reflector, the liquor in the thermometer rose 100 degrees of its scale. The papered side caused a rise of 98 degrees; the glass surface 90 degrees, and the metallic surface not more than 12°. These numbers, therefore, express the different powers of these surfaces in *radiating* caloric, as in all the experiments the effect was different, though the temperature of each surface must have been the same.

He also ascertained with accuracy the effect of different surfaces in *reflecting* radiant caloric. It was well known, that it is most completely reflected from metallic surfaces, and that it is reflected very imperfectly from a glass or blackened surface. Mr Leslie found, in conformity to this, that

when the ball of the thermometer in the focus of the mirror is coated with tinfoil, the rise of temperature which it suffers is much less than when it is uncoated : from the blackened surface of the cannister it receives an increase of temperature, instead of 100° , amounting only to 20° , and from the metallic surface, instead of 12° only $2\frac{1}{2}^{\circ}$; in other words, the ball thus covered with metal *reflects* the greater part of the calorific rays directed upon it, and therefore its temperature is not raised. The same thing is proved by substituting for a metallic mirror a glass one, (employing the thermometer in its usual state) : on presenting the most powerful radiating surface, that is the blackened side of the cube, the rise of the thermometer will be merely a visible space, the glass being capable of reflecting on the thermometer in its focus only a small part of the caloric it receives : if its surface is blackened, by spreading china-ink over it, even this slight effect ceases, and no rise is perceptible ; but if it be covered with tinfoil, the effect on the thermometer is increased to at least ten times the effect produced by the glass alone*.

The power of bodies to *radiate* caloric, and that to *reflect* it, are thus opposed to each other. A blackened surface radiates most, glass next to it, and a polished metal least ; while in the power of reflecting, the order is the reverse, the metal surface reflecting most copiously, the blackened surface least. The radiating and absorbing powers appear to be proportional, the vitreous or blackened surface absorbing radiant heat much more perfectly than the metallic one, and are inversely as the reflecting power.

Mr Leslie found, that a considerable aberration takes place in the reflection of heat, the heated body when moved from the axis of the reflector still continuing to produce its heating effect on the thermometer in the focus ;

* Leslie on Heat, p. 21.

at the distance of an inch it did not appear to be lessened, and it could be withdrawn 7 or 8 inches before the effect ceased to be perceptible. It follows from this, that the heating effect will not be in the true focus, but nearer to the mirror. And accordingly, he found, that on advancing the thermometer half an inch nearer to the reflector than the focus, the heating effect was augmented more than one-third; and even at one inch, it was greater by one-fourth; while in moving it backwards, the impression diminished rapidly *.

Another set of experiments which Mr Leslie made, relate to the effect of interposed skreens in intercepting the communication of temperature from the hot body to the mirror. From these principally he inferred his theory of radiant heat.

If a sheet of tinfoil suspended in a frame larger than the reflector be placed about two inches from the tin vessel, between it and the thermometer, the effect on the thermometer is completely intercepted, and it remains so at whatever distance the skreen is placed between the tin vessel and the reflector, and this even when the most powerful radiating surface, the blackened one, is opposed. Gold leaf, which is 600 times thinner than the tinfoil, has the same effect. If, however, instead of the metallic skreen, a pane of glass be interposed, the result is different; the liquor in the thermometer will be raised 20 degrees, estimating the entire and unobstructed effect from the blackened side of the cube at 100° . If, instead of glass, a sheet of paper be attached to the frame placed between the heated tin vessel and the mirror about two inches from the former, the rise of the differential thermometer is rather greater, being about 23 degrees.

It may be supposed, that the effect on the thermometer

* Leslie on Heat, p. 61—64.

in these experiments with the glass or paper is owing to part of the radiant caloric passing through, while another portion is intercepted. Were this the case, Mr Leslie observes, the effect ought to be the same, at whatever distance the skreen is placed between the hot vessel and the reflector, while he finds it to be dependent on its contiguity to the former: at the distance of two inches from the heated surface, the effects above stated are produced; if farther removed, the effect diminishes; and at the distance of a foot from the tin vessel, the rise in the thermometer is not one-thirtieth what it is in the first position. This he regards as a proof that the interposed skreen does not operate partly by intercepting and partly allowing the radiant caloric to pass through it, but that the calorific influence is entirely arrested, while the skreen by this acquires heat, "and in its turn displays the same energy as if it had formed the surface of a new cannister of the corresponding temperature." Hence the effect must be dependent on the contiguity of the skreen to the source of heat, and on its nature with regard to its receptive and discharging powers; when of metal, the effect is imperceptible, because a metallic surface is unfavourable to receiving caloric on the one side, or giving it out on the other; while if of glass or paper, the effect is considerable, because these substances are better fitted both to receive and discharge heat.

In confirmation of this he found, that when a substance is used as a skreen which cannot have its temperature raised, as a thin sheet of ice, it completely intercepts the effect on the thermometer. And it is still farther established by an ingenious experiment, which he supposed to be decisive. Let two panes of crown glass be coated, one on each side with tinfoil; join them together with their tin surfaces in contact, and attach them to the frame placed in the same position as in the preceding experiments, the thermometer will experience a rise equal to 18 degrees.

But let the panes of glass be joined, so as to have their tin-coatings on the outer sides, there will be no rise whatever in the thermometer ; yet in both cases the obstacle presented is the same ; and if the effect on the thermometer were owing to radiant caloric being partly transmitted, no cause could be assigned for so striking a difference, while on the principle above stated it is explained ; the metallic surfaces being unfavourable either for receiving or discharging heat, the glass surfaces being favourable for both.

From the experiments now recited, Mr Leslie draws the conclusion, that the calorific emanation is incapable of permeating solid substances. He farther infers that it is no subtle matter projected in right lines with velocity, but is merely the ambient air ; and on this assumption explains the phenomena of radiant caloric. The surface of the heated body, he observes, communicates increased temperature to the portion of air in contact with it ; this layer of air is expanded, and presses on the portion before it. This is successively but rapidly renewed ; a chain of undulations is propagated to the mirror, reflected and concentrated in its focus, and each pulsation being accompanied by a discharge of the caloric by which the expansion exciting it had been produced, the calorific effect is conveyed. When caloric is to be propagated through a solid body, it successively dilates the several portions of matter which it encounters in its progress ; but from the resistance it experiences, its expansive energy is weakened, and its progress is therefore slow. In an elastic fluid, like air, Mr Leslie conceives that there is little obstacle of this kind ; each atmospheric wave, in communicating a pulsation to the air before it, discharges with that pulsation its excess of caloric, and hence the whole is conveyed with the greatest velocity.

On this hypothesis it is obvious that the higher the temperature of the surface is from which the effect commen-

ees, the more must the atmospheric air be heated, the expansion will be greater, or will be more rapidly renewed, and hence the calorific emanation will appear to be greater. The effect of different kinds of surface at the same temperature radiating apparently different quantities of caloric, Mr Leslie supposes to arise from the more or less perfect contact of atmospheric air with these surfaces; those with which the air can come into closest contact will communicate to it the largest quantity of caloric, or will communicate it most rapidly; and from them, therefore, the calorific emanation at a given temperature will appear to be greatest: for the same reason, such surfaces will be those which absorb most readily the heat conveyed to them. And, lastly, on the same hypothesis, the effect of skreens interposed between the hot body and the mirror is explained; they always arrest a part of the calorific radiation by intercepting the chain of pulsation; but being capable, to a certain extent, of putting the atmospheric air into such a state, they still propagate it in part, and those which do so to the greatest extent must be those which are best adapted to excite originally such undulations; a conclusion which corresponds with the fact.

Were even the inference just, on which this hypothesis rests,—that no portion of radiant heat passes through a skreen interposed between the heated body and the thermometer, and that any effect apparently produced in the latter is owing merely to the temperature of the skreen being raised, and to its acquiring from this the power of discharging the calorific emanation; still the conclusion would not follow, that the air is the vehicle of communication; for it may equally be assumed, on the hypothesis of rays of caloric being actually projected, that the substance of the skreen at one surface intercepts the calorific rays; that by this its temperature is raised, and it begins to radiate caloric from the other, in quantity proportioned to

to the power of the interposed substance of absorbing and emitting caloric. The explanation on either hypothesis may in fact be the same. The effect on the thermometer, when a skreen is interposed, may be ascribed to the interposed substance receiving caloric at the one surface, and discharging it at the other, whether the caloric conveyed to it on the one side, or discharged from it on the other, be supposed to be propagated by pulsations in the atmosphere, or by actual projection of calorific particles. And on either doctrine, those substances which are best disposed to receive caloric on the one hand, and give it out on the other, such as glass or paper, will be those which will admit of the greatest effect being produced on the thermometer, while those which are least adapted to receive or to radiate caloric, as metals, will be those least capable of propagating either the pulsation, or the calorific emanation.

But farther, the conclusion which Mr Leslie drew from his experiments, and on which his hypothesis rests,—that the effect of radiant heat is not transmitted from the heated body to the thermometer through an interposed skreen unless the temperature of the skreen is raised, it now appears is not just. Mr Leslie's facts no doubt prove that the thermometer may be affected by the temperature of the skreen, as in the case of the compound skreen with its glass surfaces, and this more especially, as Dr Maycock observed, when a single mirror is used, as the skreen is then at no great distance. And also when the temperature of the radiant body is not high, the effect from the direct transmission may be so inconsiderable as not to be apparent, particularly when it is counteracted by a low temperature in the skreen, as is the case in Mr Leslie's experiment of employing a sheet of ice. But these results do not at all invalidate the reverse proposition, that the thermometer may be affected by transmission through the skreen, independent of any elevation of temperature in the latter. And

that this is actually the fact is proved by the experiments of Maycock, Prevost and Delaroche, already stated. Now, as the skreen can only act if the air is the medium of the conveyance of radiant heat in proportion to its elevation of temperature, this fact is altogether subversive of Mr Leslie's opinion, while it is sufficiently conformable to the doctrine that rays of caloric are projected from the heated body.

Neither are the other phenomena of radiant heat satisfactorily explained on the hypothesis that the air is the medium of communication. The leading phenomenon, the velocity of communication, appears in particular to be imperfectly accounted for. Mr Leslie admits, that it cannot be supposed, that a succession of heated particles of air move from the hot body, and impinge on the body the temperature of which is raised. Neither is it imagined, that by a chain of undulations, the portion of air heated and expanded at the hot surface changes its place, is moved forwards, reaches the thermometer, and is succeeded by a new wave of heated air, which observes the same motion. The supposition is, that by the heated body, the air is thrown into oscillations or undulations; that these, continually renewed at its surface, are propagated in a right line, and that at each undulation the caloric is discharged, so as to be conveyed forward with the same velocity *. But, while such undulations might be excited, by what agency is this transfer of caloric effected? Suppose a layer of air to receive heat from the hot body, and to be expanded, from this expansion it may press on the contiguous layer; but it seems no necessary or even probable conclusion, that while it impresses this motion, it shall, at the same time, discharge the heat it had received: Or, if there is any necessary connection between these events, in consequence of which the one shall accompany the other, how is the

* Experimental Inquiry, p. 242.

slow communication of caloric through aërial fluids to be explained ?

Lastly, Mr Leslie's explanation is incompatible with the results of the experiments of Herschel and Englefield, as to the existence of a calorific matter in the solar rays. These prove the existence of radiant caloric as a distinct matter, capable of rapid projectile motion, and must be regarded as affording proof of the truth of the common opinion ; or at least they prove that rays may exist analogous to light in their physical properties, capable of exciting heat without illumination, and such rays may certainly be projected from heated bodies.

There is still, however, some difficulty with regard to the common theory of radiant heat. The existence even of caloric as a distinct material substance is doubtful, and were it admitted we never clearly trace it in an insulated state. It exists always in other bodies ; it remains quiescent in them while temperature is in equilibrium ; when this is subverted, it is conveyed, by direct communication by some medium, from the hotter to the colder body, proportional to their difference of temperature ; and there is some difficulty in conceiving any cause how a portion of it should be discharged in a state of rapid projectile motion. The relation which to a certain extent is apparent between radiant heat and light adds to the difficulty. The calorific rays which exist in the solar beam, though incapable of producing illumination, have all the physical properties of the rays of light, observe the same laws of reflection and refraction, and are only inferior to a certain extent in their power of penetrating transparent bodies ; hence the opinion may be advanced as not improbable, that they are of the same nature as light, only with less projectile force, or existing under some other modification which renders them incapable of affecting the organ of vision. From these solar calorific rays, there is a kind of transition to the rays projected from heated bodies, displayed in the fact, that the

latter differ in their projectile power, according to the temperature at which they are thrown off, those discharged at a high heat penetrating transparent media with more facility than those which emanate at a lower temperature. We thus, in some measure, trace the gradation into quiescent caloric; while the facts, on the one hand, that the discharge by radiation from bodies reduces their temperature, and, on the other, that the whole excess of heat in a body may be abstracted from it without any radiation by direct communication to another, equally prove that the principle discharged by radiation and by slow communication is precisely the same. Yet caloric in the state in which it remains in bodies producing temperature, and its effects, expansion, fluidity, &c. is so different in all its laws from light, and there is so much obscurity with regard to any conceivable operation by which it should assume these different modifications, that the whole subject must be regarded as very imperfectly understood. Dr Hutton advanced an hypothesis, that radiant heat is light in a state incapable of exciting illumination, founded on the inference, that as the heating power of the different species of visible light is not proportional to their power of exciting vision, there may be a species of light capable of exciting temperature, without being luminous *. This, however, is vague; it does not account for the relation of radiant caloric to quiescent caloric; nor for the fact, that radiant caloric has none of the chemical properties of light; and it is even doubtful if light apart from caloric has any heating power. Were the materiality of caloric established, the hypothesis might not be an improbable one, that the calorific rays are composed of light and caloric; that this combination may take place in different proportions, so as to give rise to different degrees of energy predominant in the one or the other, and may extend even to the different rays of visible

* Hutton on Light.

light, which differ in the degree in which they excite heat. But all such speculations, it must be acknowledged, are deficient in precision, and rest on no satisfactory evidence. The subject will fall to be farther considered under the history of light.

From the experiments I have stated, it appears, that caloric is diffused over matter in two modes. One portion is thrown from the surface of bodies in right lines, with the greatest velocity, while another is more slowly diffused, by communication from particle to particle, until an equilibrium of temperature is established.[§]

It is of importance to discover what is the relation between these two modes. By comparing the experiments on the radiating powers of bodies, with those on their conducting powers, it appears to me that the proposition, that they are inversely as each other, is nearly just. Thus the metals are the best conductors, but they are least powerful in radiating; glass radiates powerfully, while it conducts imperfectly. A spongy covering diminishes the conducting power, while it augments the radiation. Nor is there merely this general coincidence; it is farther confirmed in more minute differences. According to Mr Leslie's experiments, the radiating power of lead being as 19° , that of iron is 15° , and of tin 12° *; but according to the experiments of Ingenhouz, already quoted, and which, in determining this question, are to be preferred to Richman's, as the conducting was ascertained apart from the radiating power, lead is the worst conductor, iron is superior to it, and tin again is superior to iron.

It is difficult to discover what proportion the caloric discharged by radiation from a body suffering reduction of temperature bears to that which it gives out by slow com-

* Inquiry, p. 78. 79.

munication. On this interesting subject, some experiments have been made by Leslie, and some similar have been added by Rumford.

That the slow communication of caloric to the surrounding medium has an important share in the cooling of bodies, is evident from the fact, that the celerity of cooling is different, according to the nature of that medium; being greater or less, as the matter in contact with the hot body is a better or worse conductor of caloric. A thermometer at a high temperature being suspended in the Torricellian vacuum, the time of its cooling, from 190° to 68° , was found by Rumford to be $10' 12''$. When surrounded with atmospheric air confined in a vessel having the same space as the vacuum, the time of cooling the same extent was only $6' 11''$. If plunged in water, it would, from the general result of his experiments, have cooled in $1' 57''$, and in quicksilver in not more than $36''$ *. And in these cases it is also found, that the different substances have suffered different augmentations of temperature, and have therefore influenced the cooling by their different conducting powers. Here it is obvious that the surrounding matter, though it might impede the radiation, has on the whole accelerated the cooling.

The same fact is demonstrated by the effect of a current of air in accelerating refrigeration. Mr Leslie exposed two tin globes, filled with warm water, the surface of one being painted with lamp-black, that of the other being uncovered, to air in different states of motion. When exposed to a gentle breeze, the unpainted globe lost half its heat in 44 minutes, the painted one half its heat in 35'. When exposed to a strong breeze, the times were 23' and $20\frac{1}{4}'$, and to a vehement breeze only $9\frac{1}{2}'$ and $9'$ †. The

* Rumford's Essays, vol. ii. p. 403, 423.
Inquiry, p. 271.

atmospheric current could not accelerate the radiation, but it would the slow abstraction, by removing more quickly the heated air, and applying a fresh portion at a lower temperature.

The effect, on the other hand, of the radiation from a hot body on its cooling, has been ascertained by Mr Leslie, by observing the time of cooling in vessels, the surfaces of which radiated unequally. A hollow globe of tin, filled with warm water, was exposed to the air of a room, the temperature of which was 15 of the centigrade scale; it sunk from 35° to 25° of that scale, in 156 minutes. It was coated with lamp-black, and on repeating the experiment, the time requisite for the same extent of cooling was only 81 minutes. The experiment shews clearly the superiority of radiation to slow evolution in reducing temperature, since when the globe was covered with a substance which is a bad conductor, instead of cooling more slowly, it cooled faster, from this covering promoting radiation.

This proportion, however, will not be the same at all temperatures. The cooling of a body in atmospheric air is accelerated by the current formed from the expansion the air suffers by its temperature being raised. Now, at high temperatures, the contiguous air being more quickly heated than at lower temperatures, this current ascending from the heated body will be more rapid, and will therefore have a greater effect in reducing its temperature. Accordingly, by repeating the experiment at a higher temperature, (80 degrees above that of the surrounding atmosphere,) Mr Leslie found the proportion different: the respective rates of cooling of the unpainted and the painted ball, which by the former experiment were as 13° to 25° , were now as 13° to 19° ; and from the two he established the general result, "that at low temperatures the portion of heat dissipated from a painted surface by the repetition of aerial contact, is somewhat

less, and in high temperatures considerably greater than what is spent by radiation *.

Similar differences are found to exist, when experiments are made on a metallic vessel, and on the same vessel coated with isinglass or covered with paper, or on a thermometer, with its bulb uncovered, and covered with gilding. And, lastly, the general effect of radiation in cooling bodies is shewn by the striking fact, that the peculiar nature of the surface has no effect on the celerity of cooling, when the body is immersed in water; the unpainted and the painted globe, for example, it was ascertained by Mr Leslie, losing their heat in water with the same facility †, the radiation of caloric not taking place, when the body is immersed in a liquid, and hence its cooling must be effected entirely by the slow evolution of caloric, and must be dependent partly on the conducting power of the fluid, and partly on its expansibility and mobility, by which its internal motions will be regulated.

The effect of these circumstances in accelerating refrigeration, affords applications of importance in practical chemistry, and some singular facts with regard to it have been discovered by Mr Leslie, particularly on the times of cooling in vessels, the surfaces of which are variously altered ‡.

A tin vessel filled with boiling water, cooled from 60 to 30 degrees of the centigrade scale in 31 minutes. When the sides were rubbed with quicksilver it cooled to the same extent in 78'. The clean instrument sunk from 30° to 15° above the temperature of the air of the room in 108'; when rubbed over with oil in 87'; and when covered with bibulous paper soaked in oil in 58'. The metallic vessel filled with warm water sunk from 20° to 10° above the temperature of the room in 117'; when covered

* Inquiry, p. 276.

† Ibid. p. 316, 317.

‡ Ibid. p. 333.

with a pellicle of isinglass, it cooled more quickly, and that with a celerity proportioned to the thickness of the pellicle: with one calculated to be the 50.000th of an inch thick, it sunk to the same extent in 101', with one the 10.000th in 82', with one equal to the 1.000th in 63', and with one equal to the 300th in 61'. These results are striking, since the coverings given to the surfaces must have impaired the conducting faculty, but this was more than compensated for, by the increase they gave of radiating power. If, however, these additional coverings be made too thick, they may counterbalance the increased radiation, by acting as an imperfect conducting medium. This is evident from an experiment of Pictet, in which the bulb of a thermometer, blackened by being held over the flame of a candle, was more quickly heated than when clear, but instead of cooling faster, it cooled more slowly, in the proportion of 5 to 6, the thickness of the covering impeding the discharge by communication, more than it augmented that by radiation.

Similar results were established by Rumford. Thus a metallic cylindrical vessel, with its sides bright, and filled with warm water, requiring 55 minutes to cool a certain extent, a similar vessel, when its sides were covered with linen, cooled to the same extent in $36\frac{1}{2}$ minutes; when covered with a coating of glue, it cooled in $43\frac{1}{4}$ minutes, and when an additional coating was put upon it, in $37\frac{5}{6}$. Varnishing the surfaces had the same effect, the maximum being at 4 coatings, when it cooled in $30\frac{1}{4}$ minutes. A covering of lamp-black caused it to cool in 34*. His experiments appear also to prove, that water in vessels of different metals cools with the same celerity. His standard vessel was of brass; and repeating the experiment with it covered with gold and silver leaf, and in

* Philosophical Transactions for 1804, p. 90, &c.

similar vessels of lead and tinned iron, the times of cooling were in all of them the same *. He concluded that the different metals have the same radiating power; but even admitting this, they differ in conducting power, and this ought to give rise to a difference in the celerity of cooling. It appears, too, from Mr Leslie's experiments, that the metals differ in their radiating power, and by this the results must be varied. Perhaps these experiments throw light on each other. We have seen reason already to conclude, that the radiating is inversely as the conducting power, and they may therefore counterbalance each other; so that in vessels of different metals, the times of cooling may be nearly the same. The assertion, however, that the different metallic vessels allow water to cool with the same celerity, is inconsistent with the experiments of Richman already quoted, on the celerity with which the thermometer cools, when its ball is incased in globes of the different metals.

The applications of the above facts, as suggesting the means of accelerating refrigeration, are obvious. Some have been particularly pointed out by Count Rumford. Polished metallic surfaces being those which radiate the least quantity of caloric, in cases where it is wished to prevent a liquid from cooling quickly, the end will be better attained by confining it in a metallic vessel, the surface of which is bright, than if it were covered with any matter, as, on the supposition of impairing its conducting power, might be done. On the other hand, in order that a liquor may cool as speedily as possible, the external surface of the vessel should be painted or blackened. Metallic tubes, for conveying or confining steam, without condensing it, as those used in the steam engine, should be kept clean and bright on their external surface, while, if our object is to condense the steam quickly, as in heat-

* Philosoph. Trans. for 1804, p. 111.

ing rooms by it, they ought to be painted or covered with any substance which radiates caloric abundantly*.

The times of refrigeration of bodies were found by Mr Leslie to be different in different elastic fluids, and in the same air in different states of density. In reducing temperature, oxygen and nitrogen gases appear to be nearly equal. But carbonic acid gas abstracts the heat from a vitreous surface about an eighth part slower, and from a surface of metal one-fourth slower than common air. Hydrogen gas abstracts it much more rapidly; its power in taking it from a vitreous surface is more than double that of atmospheric air; and from a surface of metal is nearly four times greater. When the elastic fluid is rarefied, its power in reducing temperature is diminished †. These differences have been made the subject of experiment by Mr Dalton ‡, and similar results established, as is shewn by the following table. A thermometer cooled in

Carbonic acid gas, in	-	-	-	112''
Sulphuretted hydrogen, nitrous oxide, and olefiant gas,	100''	†		
Common air, azotic and oxygen gas,	-			100''
Nitrous gas,	-	-	-	90''
Carburetted hydrogen or coal gas,	-			70''
Hydrogen,	-	-	-	40''

In another table, the power of air in cooling bodies, as connected with its density, is shewn.

Density of the air.	Therm. cools in
2 - - -	85''
1 - - -	100''
$\frac{1}{2}$ - - -	116''
$\frac{1}{4}$ - - -	128''
$\frac{1}{8}$ - - -	140''
$\frac{1}{16}$ - - -	160''
$\frac{1}{32}$ - - -	170''

* Philosophical Transactions for 1804, p. 177.

† Inq. p. 483. ‡ New Syst. of Chemical Philosophy, p. 118.

From the effect on the time of refrigeration, in elastic fluids, on a metallic and vitreous surface, Mr Leslie infers, that the differences among them in causing refrigeration depend principally on their different conducting powers. The discharge of heat from a hot body by radiation appears to be the same in hydrogen gas and in atmospheric air, and is probably the same in all airs.

From the difference of calorific effect produced by radiant heat on a vitreous and on a metallic surface, Mr Leslie has adapted a peculiar arrangement of his differential thermometer, to form what he has named a Pyroscope, or instrument capable of measuring the intensity of the heat discharged from a fire. It consists in having one of the balls coated with thin silver leaf, while the other remains uncoated. The radiant heat is in a great measure reflected from the metallic surface, while it is absorbed by, and produces the usual calorific effect on the vitreous surface; the air therefore in the glass-ball is heated, and the descent of the liquor in the stem which its expansion produces, gives a measure of the intensity of the radiant heat. The instrument is equally adapted to measure the impressions of radiant cold.

WITHOUT separating the effects of the various modes in which the temperature of a body is reduced, it is of importance to know the law it observes, and accordingly this subject—the actual rate of cooling of a body in any medium, has often been the subject of investigation. It is obvious, that *different* bodies will cool with different degrees of celerity, when placed in the same medium; and likewise, that the same body will cool with different celerities in *different* media. But, independent of such comparative differences, what is the rate of cooling in any

body in any medium, or what is the law it observes in giving off its caloric?

It could not escape observation, that the greater the difference between the temperature of a hot body, and that of the surrounding medium, the more caloric does it give out in a certain time, and that it communicates less, or cools more slowly, the nearer its temperature approaches to that of the matter around it.

Newton seems first to have investigated the law by which this is regulated *. From marking the changes of temperature which a mass of iron, which had been raised to a red heat and exposed to the atmosphere, suffered in certain times, he concluded, that the quantities of heat lost by a body in small portions of time are proportional to the excess of heat subsisting in it, or to the excess of its temperature above that of the surrounding medium. Hence, taking the times in arithmetical progression, the decrements of temperature will be in geometrical progression; and the heats remaining, considered as the differences between the temperature of the body and of the surrounding medium, will observe the same law. This law has been generalized, and applied equally to the heating of a body, by Richman, in consequence of his own numerous experiments, and those of Kraft, and expressed in the following terms: In the heating or cooling of a body exposed to a medium, of which the temperature is constant, the times being in arithmetical progression, the differences between its temperature and that of the medium are in geometrical progression †. According to this law, therefore, if a body be supposed to have an excess of temperature above the surrounding medium equal to 10 degrees, in cooling, suppose that the first minute it loses one degree, the reduction the second minute

* Philosophical Transactions abridged, vol. iv, p. 3.

† Novi Comment. Acad. Petropolit. t. i, p. 174.

will still bear the same proportion to the remaining excess; or considering this now as 10° , it will be $\frac{1}{10}$; and thus proceeding, the tenth part of what remains being evolved each time, the heat given out must be uniformly diminishing, because the excess itself, of which it is a constant part, is always becoming less.

Martine stated, in opposition to this, as the result of observations, "that the decrements of heat are partly equable, and partly in proportion to the subsisting heats." And therefore in cooling, taking the times in arithmetical progression, the decrements of temperature may be resolved into two series;—in the one, and that the most important, they are in proportion to the heats themselves, or in geometrical progression; while in the other, and less important series, the decrements are as the times, or are always uniform, that is, equal quantities of heat are lost in equal times*. This conclusion was formed by Martine principally from the consideration, that were the decrements in geometrical progression, no two bodies once unequally heated can ever arrive at a perfect equality of temperature; nor could any body heated above the temperature of the surrounding medium ever truly arrive at that medium. These corollaries may however be theoretically true, though, practically, the differences in temperature, in both cases, must at length become so minute as to be inappreciable. The experiments by which Martine endeavoured to support the view he gave, were made with the complicated pyrometer of Muschenbroeck, and being obviously inaccurate, no reliance can be placed on any conclusion drawn from them. The law of Newton, therefore, appears to be just, and, in particular, it appears to be perfectly accurate where small differences of temperature are observed.

It is so, however, only while the condition holds of the temperature of the medium being constant. If the mo-

* Essay on the Heating and Cooling of Bodies, p. 55.

tion of the medium is confined, as its temperature will then increase as it receives caloric from the hot body, the cooling of the latter will be no longer in equable proportion.

IN concluding the consideration of this part of the history of caloric, I have to take notice of a singular phenomenon, that of the apparent radiation of cold.

It was first observed by the Florentine Academicians. They describe their experiment in the following manner : “ We were desirous to try whether a concave speculum, exposed to a mass of ice weighing 500 pounds, would reflect any sensible degree of cold on a very delicate thermometer of 400 degrees, placed in its focus. The result was, that the thermometer instantly sunk : but a doubt remained, whether the thermometer was acted on more by the direct cold of the ice, or that reflected by the speculum. This doubt was removed by covering the speculum ; and certain it is, (whatsoever might be the cause,) that the spirit instantly began to rise again. Yet still we will not presume positively to affirm, that this rise might not have been owing to some other cause than the taking off the reflection from the speculum, all the precautions not having been taken which might be considered necessary to secure absolute assent to the experiment.”

Pictet made this experiment by placing in the focus of a metallic mirror, a matrass filled with snow, and in that of another, at the distance of $10\frac{1}{2}$ feet, an air thermometer. The thermometer indicated a reduction of temperature of several degrees ; and on removing the matrass, the temperature rose. On rendering the cold more intense, by pouring nitrous acid on the snow, the thermometer sunk five or six degrees more *.

* *Essais de Physique*, p. 82.

Mr Leslie shewed that this radiant cold observes, in its relations to different bodies, the same laws as radiant heat. Like it, it differs in intensity according to the nature of the surface emitting it; and the difference is of the same nature. The cubical tin vessel employed in Mr Leslie's experiments, being filled with ice, and opposed to the thermometer in the focus of the mirror, the reduction of temperature was found to be least from the metallic surface, greater from the glass surface, and still greater when the surface opposed had been blackened. The effect varies, too, according as the surface of the thermometer is altered; when it is gilt, the diminution of temperature is very inconsiderable, while, when it is blackened, it is greater than when the glass surface is opposed. Lastly, the nature of the reflecting surface gives rise to similar variations. The effect is greatest from the metallic surface, less when the mirror is of glass, and still less when its surface is covered with lamp-black. The powers of these surfaces, therefore, in radiating cold, in absorbing it, and in reflecting it, are precisely the same as their powers of radiating, absorbing, and reflecting heat. Those which radiate it best also absorb it most readily, while these two qualities are opposed to the reflecting power.

The effect from interposed skreens, Mr Leslie found to be also alike. If a sheet of tinfoil be interposed, the action of the cold body on the thermometer is intercepted; by a plate of glass, or a sheet of paper, it is only diminished, more or less so, according to the distance from the cold substance; and the effect of blackened or compound skreens is similar to their effect on the radiation of caloric.

In these experiments, then, we have apparently the emanation from a cold body of a positively frigorific power, which moves in right lines, is capable of being intercepted, reflected and condensed, and of producing, in its condensed state, its accumulated cooling power; and they appear equally conclusive in establishing the existence of radiant

cold, as the other experiments are in establishing the existence of radiant heat. The hypothesis, however, of a frigorific principle, has been banished from modern philosophy, since there was no proof of its existence, independent at least of the present experiments; and the phenomena, with the exception of those which they present, are explained with more simplicity, and in a manner more satisfactory from the abstraction of caloric. It becomes therefore a problem of some interest to give an explanation, which shall accord with the doctrine, that cold is simply the negation of heat. Two explanations have been advanced; one by Pictet, the other by P. Prevost. In both, caloric is supposed to escape by radiation from the bulb of the thermometer, and to this the diminution of its temperature is ascribed.

The principle on which the explanation given by Prevost rests, is, that caloric is radiated from all bodies at all temperatures, the quantity radiated being greater as the temperature is high. When therefore a body is placed in the focus of the one mirror, whose temperature is superior to that of the thermometer in the focus of the opposite mirror, though the ball of the thermometer is radiating caloric, yet the hot body opposed to it giving out more caloric in the same mode, and this being reflected on it by the mirror, the temperature of the thermometer must rise. When both the body in the focus and the thermometer are at the same temperature, neither suffers any change, because the quantity emitted from each being the same, and the reflection and condensation by the mirrors being alike, each receives as much as it gives out. But when the temperature of the body placed before the mirror is inferior to that of the thermometer in the focus of the other, though it is still radiating caloric, the quantity is inferior to what the thermometer radiates; the latter therefore receives less than it gives, and of course its temperature must fall *.

* *Recherches sur la Chaleur*, p. 15.

This explanation appears at first view not unsatisfactory ; but it will be found deficient when applied to all the phenomena, and in particular appears inconsistent with the effects of different surfaces in radiating cold. The principle is, that the cold surface is radiating caloric towards the thermometer, only in smaller quantity than the thermometer radiates to it. Of course, of different surfaces, which at a given temperature radiate different quantities of caloric, that which radiates least must be least powerful in returning caloric to the thermometer, and must therefore have least effect in counteracting the reduction of its temperature, in other words must produce the greatest cold. A blackened surface, we have seen, is that which, at a given temperature, radiates the largest quantity of caloric, and a metallic surface that which radiates least. Were Prevost's explanation just, therefore, the blackened surface is the one which, in the experiment on radiant cold, ought to produce the least cooling effect, and the metallic surface the greatest, because the former gives off more caloric by radiation than the latter. But the fact is the reverse ; the cold being greatest when the blackened surface, and least when the metallic surface, is opposed to the mirror. This has been attempted to be obviated by the observation, that the effect of reflection by these surfaces must be taken into account. Mr Davenport, in reply to the argument I have urged, remarked, that although a blackened surface is superior in radiating power, it is inferior in reflecting power compared with a metallic surface ; while a metallic surface, though it radiates less, reflects as much as it fails to radiate. When a cannister with these surfaces, therefore, is filled with a freezing mixture, and opposed to a thermometer ; in consequence of the low temperature the blackened surface has lost a portion of its intensity of radiation ; the polished surface has lost none of its power of reflection : the two surfaces, therefore, have suffered unequal diminutions in those powers of returning

to the thermometer, which before were equal; the radiating surface has lost more than the reflecting surface, and hence the thermometer under the action of the former receives less return than under that of the latter; and it therefore suffers a greater reduction of temperature *.

But in this argument too much is ascribed to the effect of reflection, and too little to the effect of radiation. When the temperature of the sides of the cannister has been reduced by the freezing mixture it contains, the clean metallic surface has lost a portion of its intensity of radiation, as well as the blackened surface; and at any temperature the blackened surface radiates more caloric than the clean surface does at the same temperature. It returns, therefore, more caloric to the thermometer than the other does, and hence ought to produce less cold; or, at least, allowing all the effect that can be ascribed to difference of reflection, no cause is assigned why it produces a greater degree of cold †.

* Annals of Philosophy, vol. v, p. 342.; vi, 379.; vii, 224. 303.; viii, 254.

† The following statement of the argument, different somewhat from that above, has been also given me. "It may be granted to Prevost, that a surface of metal which is not capable of discharging much of its heat, may from the same reason reflect back, or refuse to receive part of the heat which is thrown upon it. And, on the contrary, that when heat is thrown upon a vitrified surface, which does not oppose the passage out of caloric from a body, it may from the same reason admit of its entrance into the body." While this may be admitted, however, and would be satisfactory if the caloric discharged from the two surfaces of the cold cannister were the same, it is to be recollected that the vitreous surface is at a given temperature discharging *much more caloric* than the metallic one to the thermometer in the focus of the mirror; and taking this into account, a *much greater degree of cold* ought certainly not to be produced from the former than from the latter.

A different explanation was proposed by Pictet. The radiation of caloric, he conceives, is owing to the equilibrium of tension in the calorific fluid, in a system of bodies, being subverted. When a number of contiguous bodies are at the same temperature, there is no radiation of caloric among them; because throughout the whole, the caloric exists in this equality of tension or elasticity, and a resistance is every where opposed to its radiating from any particular point. But if one at a lower temperature be introduced, the balance is subverted, and caloric begins to radiate from all of them, until its temperature is raised to an equality with theirs. On this assumption the experiment of radiant cold is thus explained. Suppose, says Pictet, the mirrors A and B, (fig. 39. Pl. IV,) placed in a chamber of a certain temperature, with a thermometer in the focus of the mirror A, while the focus of B is occupied by a portion of the air of the chamber. Every heated body is in a forced state, the caloric accumulated in it having a tendency to escape. If therefore the thermometer were elevated in temperature, however little this might be, its caloric would have a tendency to pass off, and it would be diffused around as a radiating emanation, a considerable portion of which falling on the mirror A, would be reflected from it in parallel rays to the opposite mirror B, and reflected again from this so as to converge in its focus. This however is prevented, if the air in the focus of B is at the same temperature with the thermometer at A; for the caloric which it contains is at the same degree of tension, and resists the escape of the latter with the same force as that which it exerts to radiate to B. But if in the focus of B, a body colder than the thermometer in the focus of A, such as a mass of ice or snow, is placed; then the equality of tension being broken, the escape of the caloric from the thermometer will take place; the presence of the cold body opens as it were a drain of heat from the whole surrounding space; this will absorb caloric more

powerfully from the thermometer, as the mirror A, in the focus of which it is, receives so large a proportion of any calorific emanation from it, and reflects this to the opposite mirror B, in the focus of which this caloric is absorbed. The ice has the same advantage in absorbing caloric from the thermometer, as a hot body placed in its situation has in communicating caloric to the thermometer; and the experiment with it differs in nothing from that with the heated ball of iron, but in the direction in which the calorific emanation moves. In the latter it moves from the heated ball by the mirror to the thermometer in the focus of the mirror A; and in the experiment with the ice, it moves in the opposite direction; the thermometer being to the ice, what in the other the ball is to the thermometer*.

In this explanation, it is not very clearly stated, how the thermometer is more powerfully acted on by the cold body, than by other bodies in the neighbourhood. The experiment, as Dr Martin has observed, is not exactly the converse of that with the heated ball; for the thermometer is not actually a hot body, compared with the surrounding air, and it does not appear clearly how it should be reduced to a temperature lower than the air which surrounds it, at least too much is left in the explanation which has been given, to be supplied by the imagination. He explains it more fully in the following manner†.

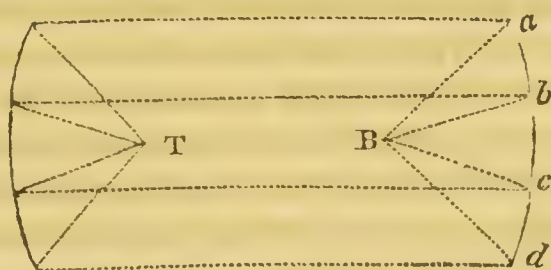
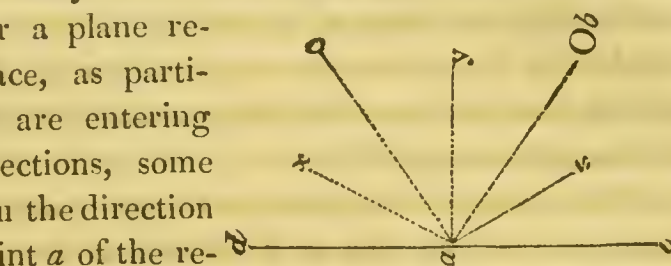
There are only two ways in which heat can be made to move in one direction through a body, as, for example, through a wire represented by the line A ——— B; one is the application of a higher temperature to B, causing the heat to move towards A by the conducting power of the wire; the other is to reduce the temperature at A, and cause a partial vacuity of heat, which will be supplied by

* Pictet, *Essais de Physique*, p. 83.

† Nicolson's *Journal*, vol. xx, p. 342.

a movement of caloric from the parts of the wire contiguous to A, and ultimately from B.

If a cold body *b*, in the annexed representation, be brought near a plane reflecting surface, as particles of heat are entering it in all directions, some must enter in the direction *a b*; the point *a* of the reflecting surface must therefore become cooler, or a vacuity of heat will be there formed. This will not be supplied by heat moving in the directions *x a*, *y a*, or *z a*, but only by that in the direction *c a*; for radiant caloric moving in right lines, and being reflected at an angle equal to its angle of incidence, if it were to come from any other direction, it could not be reflected towards the body *b*, but elsewhere, and, consequently, to join the current of heat *a b*, it must again change its course. It follows, therefore, that when a cold body is brought near a plane reflecting surface, heat will enter into that body in right lines tending to its centre; the reflecting surface will have its temperature lowered, and particles of heat will strike upon every part of it in such directions as to be thrown off in right lines to the cool body. "If we substitute concave reflecting surfaces instead of plane ones, the heat enters into the cold body placed in the focus of one mirror B from the surrounding air in all directions, consequently



every point of the surface of the mirror, *a*, *b*, *c*, *d*, &c. becomes cooled, and those points can only receive a fresh

supply in parallel rays, in a direct course from the opposite mirror, because only such rays can be thrown off towards the body B; the opposite mirror therefore becomes cool, and for the same reason the whole surface of it must be supplied by heat from the thermometer T, which consequently must become cooler than a body placed any where in its neighbourhood."

This explanation appears to be just; only it cannot be assumed, that the caloric is actually abstracted from the mirror, so that the temperature of its surface is reduced, for it would then be liable to the objection, that that kind of surface of a mirror which yields caloric most readily by radiation, that is a blackened or glass surface compared with a metallic one, should be most powerful in causing the reduction of temperature in the thermometer, in the experiment of the radiation of cold, which is not the fact, but precisely the reverse. But if the mirror be regarded simply as a reflector, this difficulty will be avoided. Now this view of its mode of action may be taken. It is not necessary to assume, that the points *a*, *b*, *c*, *d*, of the mirror are actually cooled, but only that the particles of caloric exterior to these in the direction *a* B, *b* B, *c* B, *d* B, recede from them and move in that direction, the place of these being supplied by particles moving in right lines from the surface of the opposite mirror, and the mirror acting as a reflector in turning their course.

Mr Leslie has applied his theory of aërial pulsations to the phenomenon of radiant cold; the cold surface he conceives abstracts part of the caloric of the contiguous layer of air, whence a momentary contraction of that layer follows; and pulsations, accompanied with a discharge of heat to the cold surface, and consequently in a chain from the mirror and the thermometer, are established, observing the same law as in the case of radiant heat. This explanation, of course, rests on the same grounds as his general theory.

An important application of the fact of the radiation of caloric from bodies at a low temperature, so as to produce cold compared with the surrounding medium, is that to the explanation of the phenomena of dew and hoar-frost lately proposed by Dr Wells.

Dew and hoar-frost are produced under certain conditions of the atmosphere. Dew appears in the evening, when the heat of the day has been considerable, and the atmosphere is calm : Hoar-frost is produced when the cold is greater, and when the atmosphere is not only calm but also clear. A singular fact had been observed by Mr Wilson, and by Mr Six,—that their production is accompanied with cold on the surface of the ground greater than in the atmosphere a few feet above, the difference being frequently 5, 10, or even more degrees of Fahrenheit's scale. This cold had been considered as the effect of the formation of the dew and hoar-frost, thought his conclusion involved a very considerable difficulty ; for as the transition of a body from the state of vapour to the fluid or solid form is always accompanied with an evolution of heat, it might be expected that the surface on which the dew is deposited, and still more that on which the hoar-frost is formed, would have its temperature raised, and no cause appears why it should be depressed. Dr Wells, who had made the same observation, continuing his attention to the subject, at length formed the conjecture, that the rationale of the operation is the reverse of what had been supposed,—that the cold at the surface first exists, and that, in consequence of it, the deposition of aqueous vapour from the atmosphere, constituting dew and hoar-frost, takes place. This he soon established by the fact which he ascertained by experiment, that the cold at the surface, compared with that of the air above, precedes the formation of dew, and often exists without dew being formed,—a circumstance owing to the air not containing that portion of humidity sufficient to produce a

deposition of it even when the condition of a low temperature exists. Dew, therefore, is water deposited from the atmosphere when the surface of the ground is colder than the air; and hoar-frost is the same deposition at a low temperature, so as to produce congelation; and of course both circumstances,—the presence of vapour in the atmosphere, and the low temperature, are required.

So far the investigation could have been conducted by experiments connected with the phenomena themselves. But there remained one question which could only be solved from a knowledge of the facts with regard to the escape of caloric by radiation at low temperatures. How is this low temperature at the surface of the earth produced, while the air incumbent on it is at a higher temperature? This is undoubtedly owing, as Dr Wells observes, to the radiation of heat without an equivalent return. The surface of the ground allows a portion of the heat it receives from the solar rays to escape by radiation when their action is withdrawn: hence its temperature falls; and if air holding watery vapour dissolved rest upon it, without much agitation, (a circumstance by which, by the constant renewal of warm air imparting heat, the effect would be counteracted,) a portion of this vapour will be condensed on the surface, and if the temperature is still lower, will be congealed: and the connection of this with the circumstances affecting the formation of dew and hoar-frost is established by some very striking coincidences. Thus they are formed only when the atmosphere is clear, and the occurrence of clouds interrupts or suspends it, evidently from the circumstance, that in a clear atmosphere radiation from the ground takes place most readily, and that when clouds are present, they either impede it, or return an equivalent portion of radiant heat. In like manner, any interruption in the exposure of a body to the sky, diminishes the quantity of dew deposited on it, and the quantity is greater according to the more perfect ho-

horizontal aspect. Dew forms too in very different quantities on different substances under the same circumstances; and this affords one of the most conclusive proofs of the justness of the theory. Thus, on metals, it is sparingly deposited; on glass it forms abundantly, as it does also on grass, straw, cloth, paper, and other substances of a similar kind. Now, all these substances are powerful in radiating heat, while metals radiate very imperfectly: the former, therefore, under the same circumstances, will suffer the greatest reduction of temperature; and Dr Wells accordingly found this to be the case, the difference frequently amounting to 8, 10, or even more degrees. A number of other minute facts are added confirming the same view*.

The experiments of Dr Wells prove sufficiently, that cold is produced on the surface previous to the formation of dew; and they also apparently establish the influence of a radiation to a considerable extent as the cause of this cold. But there are some difficulties attending the theory. The air incumbent on the surface at which dew is forming, is at a higher temperature than the surface itself, and this for the height of a number of feet. Now, there is some difficulty in conceiving, how, under this condition, the latter should radiate heat: the temperature at a greater height may be lower, and to this the effect is ascribed; but the interposition of a stratum of warm air, it might be inferred, would intercept the influence of this. The reduction of temperature, too, seems to be greater than can well be ascribed to radiation. Part of it must be owing to the communication of heat to the interior; and this circumstance must, to a certain extent, produce the state which actually exists, that of *decreasing* temperature in the atmosphere, as the surface is receded from to a certain height, and must give rise to a deposition of

* Essay on Dew, p. 25, 42, 98, &c.

humidity from the descent of the stratum of air thus slowly cooled. And even the different degrees of humidity deposited on different bodies may depend, in part at least, on the difference in their conducting power, as well as in the difference in their radiating power.

In a clear atmosphere during the night, it appears, that a body freely exposed to it, always becomes of a lower temperature than the surrounding air. Dr Wollaston found, that on exposing a concave metallic mirror turned upwards, a thermometer in its focus very soon indicates depression of temperature. Mr Leslie has shewn, that at all times cold is produced at the surface from exposure to a clear atmosphere; and has contrived an instrument, to which he has given the name of *Æthrioscope*, by which the effect is strikingly displayed *. It consists of the *Pyroscope*, the instrument already described, placed within a polished metallic reflector of an oblong spheroidal shape, the sentient or clear ball of the *pyroscope* occupying the lower focus, while the section of a horizontal plane at the upper focus forms the orifice; the stem connected with the ball passes through the bottom of this cup, and the scale is adapted to it beneath. In its upright position nearly all the vertical rays, or pulsations as Mr Leslie calls them, are concentrated on the ball in the focus, and the effect is measured by the movement of the liquor in the stem. When mounted on a pivot it can be turned in any oblique direction, varying a little the form of the reflector, and the position of the balls. Its sensibility is extremely great; the cold being considerable when it is exposed to a clear blue sky, and varying with every passing cloud. With regard to the theory of the operation, Mr Leslie conceives, that cold pulsations are propagated from the upper region of the atmosphere, originating in the mass of air itself. This it is not easy to admit. Pulsations may

* Transactions of the Royal Society of Edin. vol. viii.

be communicated in an elastic medium from a solid, or even from a liquid body; but it is difficult to conceive of their originating in, and being communicated from a portion merely of the elastic medium; and still more, that such pulsations arising in a higher region of the atmosphere shall reduce temperature at the surface, while the temperature of the air immediately incumbent on that surface is not reduced.

SECT. IV.—*Of the Comparative Quantities of Caloric which bodies contain. Specific Caloric.*

IN homogeneous bodies, the quantities of caloric which they contain are according to their temperatures and quantities of matter. It is found to be so on experiment, and that it should is nearly evident *à priori*; for the particles of different portions of the same matter being alike, their powers must be equal, and no cause can be imagined why one portion should have a relation to caloric different from the other, so as to require a different quantity to raise its temperature.

But there is not the same reason for believing, that with regard to heterogeneous bodies, the same law will be observed; and on making the experiment, it is not found to be the case; on the contrary, from their peculiar relations to caloric, each contains a quantity peculiar to itself. If a number of bodies of different kinds, water, oil, mercury, and others in equal weights, and at the same temperature, be exposed to a common source of caloric, they all receive it; their temperature rises with different celerities; and in a certain time they all arrive at a common temperature. It is found, however, that in rising to this they absorb very different quantities of caloric; the

water takes in more than the oil, and the oil more than the mercury. Now, it is evident, that although we suppose that at the commencement of the experiment these substances contained equal quantities of caloric; yet, at the temperature to which they are raised, they must contain unequal quantities, since in suffering this rise, each absorbed a quantity different from the others. But, in like manner, it might be shewn, by beginning the experiment at a still lower temperature, that, at the temperature from which they were raised, the quantities of caloric they contain must have been unequal; and as the same cause that disposes one body to absorb more caloric than another must be something peculiar to it, and of course must always continue to operate, it follows, that at every point in the scale of heat, different bodies contain different quantities of caloric when in the same weights and at the same temperature.

The same truth is established by communicating equal measured quantities of caloric to different bodies; we then find that their temperatures are not equally raised, but that the quantity which raises one body one degree will raise another 20 or 30 degrees.

Boerhaave began the investigation by which this important law was established. Observing that dense bodies were those which abstracted heat most rapidly from a body at a superior temperature, he imagined this might be owing to the denser mass having a disposition to contain more of this power than the other. To ascertain this, Fahrenheit, at his desire, made the experiment, which, although Boerhaave failed in drawing the proper conclusion from it, is the basis of the discovery. It consisted in first mixing together equal quantities of the same liquid,—as water, or oil, at different temperatures. Of course, the mixture immediately attained a uniform temperature; and this was found by the thermometer to be, as Boerhaave reports it, half the excess of the hotter above the colder;

that is, if 1 lb. of water at 212° were mixed with 1 lb. at 32° , the resulting temperature is 122° , the difference between the temperature of the two portions being 180° , and the half of this being taken from the hotter, and communicated to the colder, the temperature of the one therefore being depressed 90° , and that of the other raised 90° . Here, therefore, the distribution was regulated by the quantity of matter. But when equal quantities of two different bodies — of water and quicksilver, at different temperatures, were mixed together, the result was different. If the water were hotter than the quicksilver, when equal bulks of them were mixed, the temperature of the mixture was greater than the half; and, on the other hand, if the quicksilver were hotter than the water, still mixing equal volumes of them, the resulting temperature was always less than the half of the difference. When three parts of mercury by volume were mixed with two of water, at different temperatures, the temperature produced corresponded always to half the difference of the temperature in each, or was the mean between the respective temperatures, the same as when equal quantities of water were mixed together*.

From this experiment, Boerhaave inferred justly, that caloric is not distributed in bodies according to their density or quantity of matter. If it were, it is obvious, that as quicksilver is 13 times heavier than water, the addition of a quantity of mercury at a higher temperature than that of the water with which it is mixed, ought to have an effect in raising the temperature of that water equal to what the addition of 13 times the bulk of water at that temperature would have; while the experiment shews, that the effect of the mercury in raising the temperature of the water is not equal to the effect which even one measure of

* *Elementa Chemiae Boerhaave*, t. i. p. 269.

water, at the same temperature with that of the mercury, would have. It is singular, however, that he should have drawn a conclusion equally inconsistent with the experiment,—that caloric is distributed in bodies according to their volumes, or the spaces they occupy ; since it is evident, that were this the law, the temperature resulting from the mixture of equal bulks of water and quicksilver ought to have been the arithmetical mean, and it would not have been necessary to produce this mean to take three volumes of mercury to two of water.

Dr Black appears to have first perceived the error of Boerhaave, to have estimated sufficiently the value of the experiment, and drawn from it the just conclusion, that the quantities of caloric which heterogeneous bodies contain at the same temperature are proportional neither to their weights nor volumes, but are in proportions regulated by the force of that attraction which they have for this principle *. The experiments which this view suggested, were made previous to the year 1765 ; and so early as 1760, Dr Black had perceived the general fact. Wilcke, in 1771, read a dissertation before the Academy of Sciences at Stockholm, afterwards published in their memoirs, in which he announces the same principle as established by his own experiments. Dr Irvine and Dr Crawford, acquainted with Dr Black's discovery, prosecuted the subject, and subjected many substances to experiment. Some additions were made by Lavoisier, and by Gadolin ; and by the labours of these and other philosophers, the general law has been established,—*that different bodies in equal quantities, whether estimated by weight or volume, contain at any given temperature unequal quantities of caloric*, or, according to the phrase that has been used to express this, *have different capacities for ca-*

* Black's Lectures on Chemistry, vol. i, p. 79, and 504.

loric. Caloric under this modification has been named Specific Caloric or Specific Heat.

The truth of the law is evident from the experiment of Boerhaave, already stated. It is equally obvious from other examples. Thus, if we subject to experiment equal *weights* of water, of glass, of tin, of copper, and of lead, we find that these equal weights, at the same temperature, contain unequal quantities of caloric. If the water contain 1000 parts, the glass, on experiment, will be found to contain not more than 187 such parts, the copper 114, the tin 60, and the lead 42; or these respective quantities of caloric communicated to these substances will produce the same rise in their temperatures. If, again, we take equal *volumes* of them, we still find the caloric not proportional to these. If a given volume of water contain 1000 parts, the same volume of glass will contain only 448 parts, the copper 1027, the lead 487, and the tin 444. Similar differences will be found with regard to almost every kind of matter.

The general experiment, by which the quantities of caloric which bodies contain are determined, is mixing equal weights of two different kinds of matter, at different temperatures, and observing the temperature produced. If we take equal portions of the same kind of matter, one pound for example, at 50° , and another at 100° , and mix them, guarding against any error from the abstraction or communication of caloric by the vessel, or by the atmosphere, the temperature of the whole will be the arithmetical mean between the two temperatures, that is, in the present example, 75. The pound at 100 will have parted with half its excess of caloric, or 25 degrees, and this, added to the pound at 50° , will raise its temperature 25 degrees. This proves that the quantity of caloric which occasions a certain extent of change in the temperature of one portion of a body, will produce the same change in the temperature of another equal portion of the same body;

and consequently equal weights of it at any temperature will contain equal quantities of caloric *.

But, when the experiment is made with two different bodies, the temperature produced is never the mean of the respective temperatures. Thus, if one pound of water at 156° be mixed with one pound of mercury at 40° , the resulting temperature is not the mean 98, but is not less than 152° . This proves that the change of temperature produced in the one by a certain quantity of caloric, is different from that produced in the other by the same quantity; for the water in this experiment having had its temperature reduced from 156° to 152° , has lost a quantity of caloric producing in it a change of 4 degrees; but this quantity communicated to the mercury has raised its temperature from 40° to 152° , or produced a change in it of not less than 122° . The quantity of caloric, therefore, necessary to raise the temperature of one pound of water 4 degrees, is sufficient to raise that of an equal weight of mercury 112° , or the quantity raising the temperature of the former of these fluids one degree, will raise that of the other 28° . This, it is concluded, will be the case at every temperature, and therefore at any point in the scale of heat, the quantity of caloric contained in water is to that contained in the same weight of mercury as 28 to 1.

If the experiment is varied, by mixing water at a low and mercury at a high temperature, the result is the same, or the change produced in the temperature of the mercury is to that produced in the temperature of the water as 28 to 1. If one pound of quicksilver at 156° be mixed with one pound of water at 40° , the temperature produced is 44° ; the mercury has lost a quantity of caloric, which has

* This conclusion rests on the supposition, that the thermometer is an accurate measure of temperature; but even should this be doubted, the deviation cannot be such as to have an important effect. This is afterwards to be considered.

reduced its temperature 112 degrees, and this communicated to the water has raised its temperature only 4°.

In this manner, when equal weights of two different bodies are mixed together, the temperature produced is always nearer to the temperature of that body which contains the largest quantity of caloric; because it requires the largest quantity to produce a change in its temperature. The proportion is also indicated by the experiment, the comparative quantities of caloric contained in the two bodies being in the inverse ratio to the change of temperature of each by their mixture. Taking water as a substance usually employed in the experiment, and as the standard to which the others are referred, the following formula has been given. Multiply the weight of the water by its change of temperature. Do the same for the other substance. Divide the first product by the second. The quotient expresses the comparative quantity of caloric contained in that substance, the quantity contained in water being accounted 1; for each of the products giving the number of degrees which a unit of the substance would be raised in temperature, and the quantities being equal, the capacities must be inversely as the changes of temperature, that is, as the products. Or more generally, and without any reference to water being employed, but merely from two bodies being mixed in equal quantities,—multiply the weight of each body by the number of degrees between its original temperature and the common temperature obtained by their mixture. The capacities of the bodies will be inversely as the products. If we mingle the two bodies in unequal quantities, which in some experiments may be more convenient, the capacities are reciprocally as the quantities of matter multiplied into their respective changes of temperature.

When, instead of comparing the quantities of caloric which equal *weights* of different bodies contain, we compare the quantities contained in equal *volumes*, we still find,

that a difference exists. Thus, the quantity of caloric necessary to raise the temperature of a given volume of water any number of degrees, is to that necessary to raise an equal volume of mercury the same number of degrees as rather more than 2 to 1; and this consequently is the proportion between the quantities of caloric in these bodies estimated by their volumes. The comparative quantities of caloric in bodies are usually estimated by their weights, it being less difficult to ascertain these with accuracy than their volumes.

In some cases water cannot be employed, from the substance, the capacity of which is to be ascertained, exerting a chemical action, by which the existing capacity is altered, and caloric is evolved or absorbed. Dr Irvine employed the medium of a third body, generally pounded glass; adding to a given weight first of the water, and secondly of the substance whose capacity was to be ascertained, a quantity of glass of a determinate temperature, sufficient to change their temperature the same number of degrees. The capacities were then as the weights of glass added *.

Wilcke employed a method essentially the same with that now described, though in the mode of performing it somewhat different. His experiments were restricted to substances existing in the solid state. A pound of such a substance, of a metal for example, was accurately weighed; it was then suspended by a thread in a vessel of boiling water, in which a thermometer was placed, to mark the temperature with more precision. An equal quantity of water, at the temperature of 32° , was put into a tinned iron vessel. The heated body was removed from the vessel of boiling water, and suspended in the cold water. A thermometer with a centigrade scale, each degree being such that 4ths or even 8ths could be distinguished on it,

* Chemical Essays, p. 87.

was put into the fluid, and the temperature was taken when it had become uniform through the fluid, and the same as that of the solid suspended in it. The caloric given out by the hot body being thus communicated to the cold fluid, the changes occasioned in the temperature of the one by the abstraction, and in that of the other by the addition of this caloric were discovered, and the quantity of caloric contained in the body subjected to experiment compared with that of the water was easily found; the same formula applying to this method as to the preceding one, though that which Wilcke employed was more complicated *.

It is obvious, that the accuracy of these experiments depends on the assumption, that the caloric abstracted from the hot body is communicated entirely to the colder, and that the latter receives caloric from no other source. These requisites, however, cannot be perfectly attained. In the mode of mixture, if the cold substance be added to the hot one, it must receive a portion of caloric not only from it, but likewise from the vessel in which it is contained; or if the hot body be added to the cold, the caloric it gives out will not be communicated entirely to the latter, but will in part be given to the vessel. It is scarcely possible too to abstract entirely the agency of the atmosphere, which, as one of the bodies is always at a temperature superior to it, will carry off part of the caloric. The portions of caloric withdrawn from the mixture by these causes will vary according to the quantities of the substances used in the experiment,—the degree of agitation by which they are mixed, —the celerity with which different bodies part with their caloric,—their specific gravities, and their miscibility with water; and even the size and shape of the vessel, and the composition of the matter of which it consists,

* Translation of Wilcke's Paper, from the Memoirs of the Royal Academy of Sciences of Stockholm, for 1781, in the *Journal de Physique*, t. xxvi, p. 250.

will influence the result. Hence have arisen the differences in the experiments of different chemists. Dr Crawford, who made more experiments on this subject than any other chemist, and who conducted his experiments with the greatest attention, has pointed out the principal circumstances which require to be attended to. He found it necessary to determine the precise effect of the vessel on the result, by ascertaining the quantity of caloric it required to produce a certain change in its temperature; and to calculate the quantity of caloric communicated to the air, by observing the progress of cooling, and the time which elapsed before a common temperature was established; and he also adds the necessary cautions, by which the other sources of error may be best obviated*.

In the method employed by Wilcke, these sources of error have less influence. This method, however, cannot well be applied to liquids; and with regard to these, the mode by mixture is at the same time less liable to error than it is with regard to solids, as two fluids can be mixed with more facility than a solid or a liquid, and their common temperature is sooner formed.

Another method of estimating the comparative quantities of caloric has been employed, founded on the fact, that ice or snow, in melting, absorbs a uniform quantity of caloric: and therefore, by placing a hot body in contact with ice, so that the whole of the caloric it gives out in the reduction of its temperature to 32° , shall be communicated to the ice, we may determine, from the quantity of water formed, the portion of caloric which has been communicated. Wilcke, to whom this fact was known, conceived the idea of thus employing the melting of ice or snow, as a method of comparing the quantities of caloric in bodies; all that is necessary, says he, being “to find, by experiment, how much soft snow is necessary to cool different bodies,

* Treatise on Animal Heat, p. 96.

from a certain determined temperature, to that of melting snow or ice; for the whole heat which the body loses in this reduction ought to be found in the melted snow; and thus the quantity may be known from the quantity melted or the quantity of water produced *." In attempting, however, to carry it into execution, he found unexpected difficulties, principally in determining, with accuracy, the quantity of water produced, as much of it remained mixed with the portion of unmelted snow; he relinquished it, therefore, for that already described.

Lavoisier and Laplace, however, directed their attention to this method, and contrived an instrument, the Calorimeter, by which the experiment can be performed. It consists of three vessels, A, B, C, adapted to each other, and inserted the one within the other, so as to leave a cavity between the sides of each. The innermost A, is a cage of iron net-work designed to contain the body to be subjected to experiment, and supported by bars attached to the internal cavity of the second or middle vessel B. This is designed to contain the ice, broken into small pieces, and supported on an iron-grating at the bottom, through which the water filtrates, and is conveyed off by a pipe with a stop-cock, which comes from the bottom of the vessel. It has a double cover capable of containing ice; the under part of this being perforated, so that the water from the melting of any of the ice it contains may drop into the cavity itself. The third, or outer vessel, C, is similar in its construction to the second, and is filled with pounded ice and water when the experiment is to be performed, in order to prevent any heating or cooling agency of the atmosphere on the ice in the middle vessel, and preserve a steady temperature of 32°. It also has a double cover D, containing pounded ice, to serve the same purpose, and a tube and stop-cock by which the water when it accumulates can be withdrawn.

* Journal de Physique, t. xxvi. p. 258.

In performing the experiment with this apparatus, the body to be operated on is heated and suspended in the innermost cavity, the middle cavity having been previously filled with pounded ice pressed down, and drained so that no water remains. The caloric it gives in falling to 32° , is communicated to the ice in this cavity, and melts it. Lavoisier and Laplace calculated, that one pound of ice in melting absorbs a quantity of caloric which would raise the temperature of water 135 degrees of Fahrenheit. By withdrawing the quantity of water produced, and weighing it, it was easy on this principle to ascertain the quantity of caloric which the substance in the reduction of temperature it had suffered had given out; and by repeating the experiment on different bodies, the comparative quantities of caloric they evolve in passing from one temperature to another, and of course the comparative quantities they contain, were determined. Liquids were introduced in a glass matrass; the quantity of heat which the glass would give out being ascertained by a previous experiment; and Airs were operated on, by passing them through a spiral tube, fixed in the middle vessel, a thermometer being placed at each extremity of it, to ascertain the temperature of the air as it entered and passed out*.

These experiments require to be made at a temperature near to 32° , as, below that, the contents of the outer vessel may be frozen, be cooled, and abstract caloric from the middle vessel; and when much above it, the air included in the instrument, being heavier than the external air, descends, issues by the tube at the bottom through which the water runs off; and thus a current of air is formed, which communicates heat to the ice. Even with every precaution, however, it appears, that important sources of error attend the apparatus. Two circumstances were pointed out by Mr Wedgwood as influencing the results.

* Mémoires de l'Acad. des Sciences, 1780.

The first is, that part of the water formed by the melting of the ice is retained by capillary attraction in the interstices of the unmelted ice; and hence the quantity that passes off by the tube, at the bottom of the apparatus, is not the proper measure of the quantity actually produced. The other, that the operations of thawing and freezing actually go on at the same time, part of the water which is melted in the upper part of the middle vessel, in filtering through the ice, returning to the solid state, so that in the lower parts of the apparatus, the fragments of ice thrown in loose are frozen together, and the passage through the loose ice is soon nearly filled up *; an effect no doubt owing to the cohesive attraction exerted by the surfaces of the fragments of ice to the water at 32° . These circumstances render it very doubtful, whether this method is equally accurate with the more simple mode of mixture at different temperatures.

Meyer proposed another method of ascertaining the comparative quantities of caloric in bodies, founded on observing the times equal volumes of them require to cool through a certain interval of the thermometric scale; these times being as their capacities estimated by the volume, and hence, if divided by the specific gravity of the substance operated on, giving the capacity as estimated by the weight †. The same method has been employed by Mr Leslie ‡; and Mr Dalton has considered it as susceptible of great precision, and so far preferable to the mode of mixture, that the results are independent of any inaccuracy of the mercurial thermometer ||. The principle, however, on which it rests, is not just, for the cooling of bodies depends on other circumstances than their capacities.

* Philosophical Transactions, vol. lxxiv. p. 376.

† Annales de Chimie, tom. xxx, p. 46.

‡ Inquiry, &c. p. 340 and 548

|| System of Chemical Philosophy, p. 55.

It is influenced both by their radiating and conducting powers. Any error, indeed, from the former may be avoided by the mode in which the experiment has been performed by Leslie and Dalton,—giving the same external surface to the body while cooling, by including it in a glass globe. But it is not possible to obviate entirely the latter. It is obvious, in the example of a mass of matter at a high temperature, communicating the excess of its heat to the surrounding medium, whether by the intervention of a vessel containing it, or not, that if it be an imperfect conductor of caloric, the caloric passing more slowly from the internal mass to the surface, the time of cooling will be longer than if it were the reverse, the capacity being the same. In liquids, too, the degree of mobility and expansibility influencing the motions of their parts, must influence their times of cooling. Hence an accurate conclusion cannot be formed of the quantities of caloric which a body evolves, as its temperature falls, compared with that given out by another, by observing their respective times of cooling, but only by measuring these quantities by the effects they produce on another body to which they are communicated.

The preceding observations apply principally to the methods of ascertaining the comparative quantities of caloric in bodies which are solid or liquid. With regard to the mode of determining the specific heats of ærial fluids, there are greater difficulties. In observing the changes in the temperature of an æriform fluid, and the corresponding change in the temperature of a body with which it is put in intimate contact, and thence inferring the capacity, the sources of error, which always, to a certain extent, attend the experiment, must, from the small quantity of matter in such volumes of the gases as can be submitted to trial, have a greater influence on the result. The quantity can scarcely exceed a few grains in weight; from this so little heat can be imparted to the contiguous matter, that diffe-

ences in the quantities, communicated by different elastic fluids, must be very minute, and much more must be due to the effect of the containing vessel; hence, as Dr Crawford justly observed, the errors of the observations will bear a considerable proportion to the differences which are to be ascertained. In his experiments, the differences from the *volumes* of gases employed seldom exceeded the $\frac{1}{100}$ th of a degree of Fahrenheit's; and although he used a thermometer of such a construction, that $\frac{1}{100}$ th marked on its scale was as distinct as an entire degree on that of the thermometer in common use, yet even this difference is so small, that the results cannot be free from all suspicion of inaccuracy. He employed, however, every precaution to obviate this; and the method which he principally used seemed well calculated to ensure accurate results. His apparatus consisted of two separate vessels of thin brass, of the same form, capacity and weight, attached to a cross bar, so that both could be equally exposed to the same source of heat, conveyed by means of cylinders surrounded with warm water, and could be equally plunged into similar quantities of cold water, sufficient to cover them: The one vessel was filled with the air submitted to trial; in the other a vacuum was formed. Both were heated to the same point indicated by a delicate thermometer in each, and were then plunged into the similar quantities of cold water: the elevations of temperature in these were observed by thermometers equally delicate; and the temperature communicated by the exhausted vessel, being subtracted from the temperature communicated by the vessel filled with air, the difference shewed the temperature communicated by the air alone; whence, comparing this with the reduction of temperature in the air, the specific heat or capacity of the latter could be ascertained. The accuracy of the method could farther be confirmed by introducing atmospheric air into the one vessel, and the gas designed to be operated on into the other, and observing the compara-

tive effect. And the certainty of the result was established by a very decisive test, that when the same air was submitted to experiment, the same results were obtained : it was only when different airs were used that a difference was found, a proof that this had been owing to some difference in the airs themselves. His first observations were confirmed even by experiments with thermometers, in which each degree of Fahrenheit's scale was divided into 50 equal parts ; the differences observed, too, were constant in repeated experiments ; and being from equal volumes of the gases, they of course are much more considerable, when reduced to equal weights, according to which the capacities of aerial fluids are estimated, so much so, that, as Dr Crawford himself justly observed, were the heats communicated to water, by equal *volumes* of the different gases, the same, still from the differences in their specific gravities, differences in their capacities for caloric would be established. And still more if the real differences are the reverse of those he assigned, as has since been maintained, ought the diversity of effect conformable to this to have been apparent.

The subject has more lately, however, been submitted to experiment by Messrs Delaroche and Berard, who have considered Crawford's results as altogether inaccurate. The method they employed consisted in passing a current of gas, at a certain elevated temperature, from a gazometer, through a spiral tube placed in a cylinder of thin copper, filled with water and closed. It is known that if a constant and uniform source of heat be applied to a body insulated in the atmosphere, this body will gradually rise in temperature until it attain a point at which it will give out to the surrounding air as much heat as it receives, and at this point it will remain stationary. It is also known, (conformable to the law which has been already stated,) that the quantity of heat lost each instant by a hot body suspended in the atmosphere is propor-

tional to the excess of its temperature above that of the circumambient medium. If, therefore, a regular current of gas, at a certain constant elevated temperature, pass through the spiral tube in the copper vessel with the included water, this may be regarded as a constant source of heat, the vessel being the body discharging it. If the experiment be repeated with different gases, each will raise the temperature to a certain fixed point, which will remain stationary, and it will follow, from the above principles, that the quantity of heat communicated to the cylinder, by each in a given time, will be proportional to the excess of that stationary temperature above that of the surrounding medium. The comparative specific heats of the different gases will thus be ascertained. The necessary precautions were of course to be attended to, of maintaining a constant current of gas at an uniform temperature, and of ascertaining, by delicate thermometers, the temperature of the gas as it enters and escapes, and the temperature of the vessel through which it passes, as well as to appreciate the influence of any other causes which might affect the temperature*.

The results obtained by these chemists by this method, assign specific heats of the different gases totally different from those established by the experiments of Crawford. Instead of being in general superior to water as a standard, they are, with the exception of hydrogen, inferior; and instead of oxygen gas having a great specific heat, it is comparatively low. A table of the precise results will be found with the other tables on this subject at the end of the chapter.

The determination of the accuracy of these results, compared with Crawford's, is a point of considerable importance; for if admitted, they invalidate some of the most

* Nicolson's Journal, vol. xxxv, xxxvi. Thomson's Annals, vol. ii.

important conclusions in modern chemistry, particularly the theory of the evolution of heat in combustion, and the theory of animal heat by respiration, as well as some generalizations in the relation of caloric to temperature. In comparing them with Dr Crawford's, they do not appear to me entitled to any preference. The only deficiency that can be objected to the latter, is that, derived from the smallness of effect whence the conclusion was drawn, arising necessarily from the small quantity of air that could be operated on. But this is more than compensated by the simplicity of the apparatus, the precautions which were employed by Crawford to augment the apparent change, and to insure accuracy to the result, and the superiority of the principle of the method itself,—that of inferring the capacity from the change of temperature in one body compared with the other, from the caloric communicated to the former, and abstracted from the latter. The apparatus of the French chemists is extremely complicated, and the influence of a variety of circumstances required to be regulated or estimated, particularly the uniformity in the current of gas, the constancy of its temperature, the accurate determination of this temperature as it enters and escapes, the effect of moisture, and the influence of the surrounding medium liable to be affected by external causes arising from the experiment itself. Some of these were even admitted to be imperfectly regulated. And the method, independent of these sources of error, is obviously inferior in its principle, and in delicacy of observation; for any small difference in the effect produced by a gas acting on the vessel will not be immediately or strikingly displayed by the latter: such differences therefore will not be easily observed, and by slight variations of circumstances will be liable to be materially modified. It was accordingly found difficult to raise the temperature to its maximum by the transmission of the gas, and preserve it so for a sufficient time, so as to de-

termine the effect with accuracy; hence a different method was followed. The process was stopped, when it was judged that the temperature of the vessel was within 0.5, or 0.7 of a degree of its maximum; then, raising by a spirit-lamp, the temperature above the maximum, and causing the current of gas to pass through till it began to cool, it was again stopped, when it was supposed that this was as near the maximum, on the one hand, as the heating was on the other: the mean between these was then taken, and considered as the point "at which the vessel would have remained stationary, if the current of hot gas had been long enough continued." Under all these circumstances it can scarcely be inferred, that the method is superior to Crawford's, but the reverse: it is both liable to more numerous sources of error, and these are less apparent, and less capable of being checked. This, too, it may be remarked, is a subject of experiment, in which no advantage has been gained by the progress of the science, so as to render the investigation more accurate now, than at a former period. It could be conducted with just as much facility and precision at the period when it was undertaken by Crawford as at present; his experiments were conducted with the greatest care; they cost the labour of years, and are certainly not to be invalidated but by a very evident and decided superiority of others.

There are also some general considerations which throw considerable doubts on the results stated by Messrs Delaroche and Berard. They find all the gases, with the exception of hydrogen, to have capacities inferior to water, and in general inferior to liquids, and approaching more nearly to those of solids. Yet in considering the progressive changes of form, it is more probable that a similarity of relation should continue to operate, and therefore that since, in general, liquids have greater capacities for heat than solids, aëriform fluids should have capacities still farther increased. The capacity of watery vapour is even found by

these chemists to be inferior to that of water, in the proportion of 24 to 1000. This not only violates the above analogy, and another equally general, that rarefaction is usually, perhaps invariably, accompanied in every body with an increase in its capacity for caloric; but in consequence of it, a very large quantity of heat ought to be rendered sensible when water passes into vapour, and a very intense cold should be produced when steam is condensed, while the facts are precisely the reverse: nor, if we admit their estimate, can these circumstances of the non-liberation of heat when water passes into vapour, and instead of it, the actual absorption of a large quantity, be accounted for, but on the vague and improbable hypothesis of combined caloric. Precisely the same difficulty occurs with regard to the formation of gases by combination. Oxygen gas by combination with charcoal passes into carbonic acid gas without any change of volume. The capacity of carbonic acid gas is, according to these chemists, to that of oxygen gas, estimated by volume, as 1.2583, to 0.9765. In this conversion, therefore, that is in the combustion of charcoal, as there is this augmentation of capacity, there ought to be a production of cold; and it is necessary to assume, on the same improbable hypothesis, that there exists in one or other of the elements a quantity of caloric chemically combined, not only to supply this difference of capacity, but to afford the high degree of heat which is actually produced. Yet these chemists themselves admit, that in all cases where experiments can be easily performed without being liable to error, when there is a disengagement of heat from the combination of two bodies, the compound has a capacity less than the mean of those of its elements. Lastly, this very estimate of the small capacity of oxygen gas, the point of most importance in the whole investigation, is at variance with a very strict and extensive analogy. All the compounds of oxygen have capacities for caloric greater than

the bases of which they are formed, as is apparent in the example of the compounds of oxygen with metals, and also with inflammables,—substances in which the estimation of the capacities can be determined without any important fallacy. This is a very general relation which can scarcely be ascribed to any other cause than to the agency of oxygen, and seems to prove, that that element contains a large quantity of caloric at a given temperature, whence it communicates the same property to the compounds in which it predominates.

On all these grounds there seems every reason to infer, that though Crawford's determinations of the capacities of the gases may not be perfectly correct, they still remain nigher approximations to the truth than any others.

Some other modes of determining the capacities of elastic fluids have been proposed. The following is by Mr Leslie. When air is admitted into a partially exhausted receiver, heat is produced from the condensation of the rarefied air. If a delicate thermometer, therefore, is fixed in the centre of a large receiver, the greater part of the air extracted, and time allowed for the apparatus to acquire the temperature of the room, on suddenly admitting air into the partial vacuum, the rarefied aerial fluid contained in it is condensed, and the temperature is raised. If the experiment be repeated with some other species of elastic fluid, the same quantity of heat will be liberated, and communicated to this gas; but it will not produce the same elevation of temperature. If the gas employed have a greater capacity for caloric than an equal volume of atmospheric air, it will suffer less alteration of temperature; and thus, by repeating experiments with the different elastic fluids, their capacities may be determined. Mr Leslie found, that hydrogen gas suffered the same change of temperature as atmospheric air; hence these two elastic fluids, in the same volume, contain the same quantity of heat.

Gay-Lussac has called in question the principle on which the method rests, that the heat evolved when a gas is admitted into a partially exhausted receiver, arises from the condensation of the rarefied air in the receiver ; for were this the cause, it must happen, that on introducing a very small quantity of gas into the receiver, as much heat must be absorbed by the rarefaction of this, as is given out by the condensation of the other ; while the fact is, that on the introduction of even the smallest quantity, there is a production of heat. He considers the heat as in part arising from the air that enters the receiver. And he obtained results different from Mr Leslie's ; the change of temperature in hydrogen gas, and in atmospheric air admitted into the partially exhausted receiver, being very different. He found, in prosecuting these experiments, that the variations of temperature produced by the changes of volume of gases are greater, as they are of less specific gravity ; whence he concluded, that their capacities for caloric, under equal volumes, are greater, as their specific gravities are less *. But this he has since considered as doubtful ; and the method, independent of the discordant results in these experiments, seems to be exceptionable, from the difficulty of rendering the circumstances sufficiently uniform.

Since different bodies, whether in equal weights or volumes, contain, at the same temperature, different quantities of caloric, there must be some cause by which this difference is produced,—something in the relation of bodies to caloric, varying in its intensity in each, by which one requires a quantity different from that required by others, to produce the same change in its temperature.

This property, whatever may be the nature of it, has been termed the Capacity of bodies for heat, or, adapting the

* Mémoires de la Société d'Arcueil, tom. i, p. 200.

expression to the established nomenclature, the capacity of a body for containing caloric. This phrase is not free from ambiguity, as it in some measure conveys the idea that caloric is contained in bodies, according to the spaces existing in them which it can fill. This, however, is not its proper sense: it merely expresses the general fact, that different bodies contain, at equal temperatures, and in equal quantities of matter, different quantities of caloric; or rather, it denotes the property by which they do so, without being understood to convey any idea as to the cause of that fact or property. The caloric thus contained in bodies in quantities peculiar to each, was named by Wilcke their specific heats, by Crawford their comparative heats. The phrase Specific Caloric is generally used to express it, and, as applied to any particular body, denotes the quantity of caloric which any weight of it at a given temperature contains, compared with the quantity which another body in the same weight, and at the same temperature, contains. Thus the specific caloric of water is said to be to that of milk as 1000 to 999.

Of the relation between this property, the agent on which it operates, and the state with regard to temperature, the following clear statement is given by Dr Crawford; the term heat as he uses it being synonymous with caloric: "The temperature, the capacity for containing heat, and the absolute heat contained, may be distinguished from each other in the following manner: The capacity for containing heat, and the absolute heat contained, are distinguished as a force from the subject upon which it operates. When we speak of the capacity, we mean a power inherent in the heated body; when we speak of the absolute heat, we mean an unknown principle which is retained in the body by the operation of this power; and when we speak of the temperature, we consider the unknown principle as producing certain effects upon the thermometer." The capacity for containing heat may continue unchang-

ed, while the absolute heat is varied indefinitely; and by every addition of absolute heat in this case, the temperature will be increased, or by its abstraction will be reduced. The temperature of a body, therefore, depends on its capacity, and on the quantity of heat communicated to it; and, from a variation of either, a change in the temperature must result. If the capacity be enlarged, the quantity of caloric remaining the same, the temperature must fall; if it be diminished, the temperature will rise, in precisely the same way as if the capacity had remained constant, and caloric been withdrawn or communicated.

It must be obvious, from the nature of the experiment by which the capacities of bodies are ascertained, that they are not absolute. We discover only how much caloric a body gives out or absorbs during a certain change of temperature; and by observing the change of temperature which the body, from which it has received, or to which it has given this caloric, suffers, we ascertain the comparative quantities necessary to produce equal changes of temperature in these bodies. But we do not learn the proportion which the quantity in each bears to the whole caloric it contains, and therefore the capacities are merely comparative. Hence it becomes necessary to assume a standard, to which the others are referred. Water is taken as this standard. Its capacity is stated at 1000, and the capacities of other bodies are stated in relation to this. Thus the capacity of hydrogen gas is 21.400; implying, that if, at any given temperature, a certain weight of water contain 1000 parts of caloric, the same weight of hydrogen gas, at the same temperature, will contain 21.400 such parts. The capacities have sometimes been estimated, by comparing bodies in equal volumes, and sometimes by comparing them in equal weights. The latter can be done with most accuracy; and it is also proper to refer the quantity of caloric contained in a body to the quantity of matter, as it is by the action of this matter on it that the

proportion of caloric is regulated. The capacities, as they relate to equal volumes, are found by multiplying the number expressing the capacity or specific caloric of any substance as estimated by its weight, by the number which denotes the specific gravity of that substance, the product being the specific caloric estimated by the volume. I have added at the end of the Chapter tables of the capacities of bodies, as ascertained on different authorities, and according to the different methods above explained.

THE question naturally occurs, To what cause is the difference in the capacities of bodies to be ascribed? or, stating it more generally, What is the nature of that property by which one body requires more caloric than another, to produce the same temperature?

The most important general fact with regard to this is, that there is a connection between the capacities of bodies for caloric, and their rarity or density. Those bodies which have the smallest capacities, are those of greatest density, such as the metals, while substances of the greatest rarity—the different elastic fluids or airs, are those which have the greatest capacities for caloric.

The capacity of a body is changed also by changing the density, its rarefaction being accompanied with an increase of capacity. This is conspicuous in those substances which are most susceptible of rarefaction, the æriform fluids. When any species of air is rarefied by the air-pump, its temperature falls, obviously from the increased rarity enabling the air to contain a larger quantity of caloric at a certain temperature; and as this caloric cannot be immediately absorbed from the surrounding bodies, the temperature of the air suffering rarefaction must be reduced. On the contrary, by compressing any æriform fluid, caloric is extricated, the capacity being diminished by the reduction of volume. The changes of temperature from these causes, it has been shewn by Mr Dalton, are greater than what

they appear to be on experiment, owing to the surface of the contiguous vessel rapidly absorbing or yielding caloric, and thus quickly checking the actual change*. To this cause also is to be referred a fact discovered by Mr Watt, and which otherwise appears anomalous, which has indeed appeared so much so to Berthollet, that he is unwilling to admit it †, “That the latent heat of steam,” (which, as we shall afterwards shew, depends on the capacity), “is less when it is produced under a greater pressure, or in a more dense state, and greater when it is produced under a less pressure, or in a less dense state ‡.”

When, by other means, the volume of a body is changed without materially altering its nature, we change its capacity for caloric. Thus the clay used in Wedgwood's pyrometer has its capacity diminished one-third, by being burnt to 120° of the pyrometrical scale, and thus reduced to about one-half of its bulk, and as it loses in weight little more than two grains in a pound, the diminution of capacity can only be ascribed to its condensation §. Lastly, when we combine substances together, if the combination be attended with an increase of density, there is also a diminution of capacity, as is exemplified in the combinations of alkohol or of sulphuric acid with water.

So far the connection appears intimate between the rarity of bodies and their capacities. These, however, are not proportional to each other. Water has a capacity to that of mercury as 28 to 1, while the specific gravity of the one is to that of the other as 1 to 13. Alkohol is less dense than water, yet its capacity is less, instead of being greater, in the proportion of 602 to 1000. Many similar examples might be stated, which prove that the capacities of bodies are not inversely as their densities.

* Manchester Memoirs, vol. v.

† Chemical Statics; vol. i, p. 415.

‡ Philosophical Transactions, vol. lxxiv, p. 335.

§ Philosophical Transactions for 1792, p. 280.

Supposing caloric to be matter, this may be ascribed to the attraction by which it is contained in bodies. Its particles on this hypothesis being mutually repellent, its tendency is to diffuse itself equally ; and did no foreign power operate, it would be contained in all bodies, the temperatures being alike, in quantities proportioned to the spaces they occupy. But an attraction being exerted towards it, modifies the law which would otherwise be observed ; and this being different in its intensity in different bodies, may give rise to the specific quantities which they contain. Accordingly, Crawford found, what is conformable to this view, that more caloric is contained at a given temperature in a certain volume of atmospheric air, than in a vacuum of the same space *.

Caloric, then, on this hypothesis, may be considered as having a tendency to diffuse itself equally over space, and of course to exist in bodies in quantities proportional to the void spaces between their particles, or rather to the distances to which, by its elasticity, and their relative force of cohesion, it is capable of separating them at a given temperature. But this is modified by the attraction exerted towards it by the particles between which it is interposed, by which it is condensed ; and the attraction, it may be presumed, being different, as exerted by different bodies, hence may arise the difference in the quantity of it contained in different bodies at any given temperature. At the same time, in the exertion of this specific attraction, we observe none of the usual laws of chemical affinity ; the phenomena attending the communication or abstraction of caloric are dissimilar to those of chemical combination ; it exists in bodies with its properties unaltered, the *quantity* they contain only being determined by the attraction they exert towards it. And the relations of this agent are so peculiar, that no analogy from ponderable

* Treatise on Animal Heat, p. 266.

substances can be justly transferred to it, nor can much confidence be given to any theory founded on such analogies. The general fact must therefore be established merely as an ultimate one, that bodies require specific quantities of caloric for the production of temperature, a fact expressed by saying that they have different capacities for caloric.

On the subject of capacities, it is an interesting question, whether they are permanent ; in other words, are they the same at all temperatures ? Will the quantity of caloric which raises the temperature a certain number of degrees at one part of the thermometrical scale, suppose at the medium temperature of the atmosphere, raise it the same number of degrees at any other, either higher or lower than this ? It is obvious that this may not be the case, but that the rise of temperature itself, and the effects by which it is accompanied, may give rise to a change in the relation ; so that, at different parts of the scale of heat, the change from the communication of a given quantity of caloric may be either greater or less than at other temperatures.

In considering this question, it is necessary to remark, that the capacities of bodies are altered when they change their forms. When they pass from the solid to the fluid, or from the fluid to the æiform state, their capacities are enlarged, and are diminished when they suffer the reverse changes : But, with this exception of change of form, are their capacities permanent or not ?

This was investigated by Crawford. The experiment he employed consisted in mixing equal quantities of the same body, at different temperatures. If the capacity at all temperatures between these were uniform, it is obvious, that the temperature formed would be the arithmetical mean ; for the quantity of caloric abstracted from the hotter portion, and communicated to the colder, would raise the temperature of the one just as much as it reduced that of the other. But if the capacity were not permanent,

if it was either augmented or diminished by a rise or fall of temperature, there would be a deviation greater or less from the mean. If the capacity were greater at a high than at a low temperature, then the temperature resulting from mixing the two portions together would be above the arithmetical mean, as the quantity of caloric yielded by the hotter to the colder would not reduce its temperature so much as it would raise that of the other; and, on the other hand, if the capacity were less at the high temperature, the resulting temperature would be below the mean.

To determine this, Crawford mixed equal portions of hot and cold water; the temperature of the mixture was the mean between the two; and hence he concluded, that the capacity of water is permanent in all temperatures between its freezing and boiling points. He extended his experiments to other substances, especially to the metals, and some of their compounds; and though the results did not correspond accurately with the supposition of a permanence of capacity, they agreed more nearly with it than with any other: "Hence we may conclude in general," he adds, "that the capacities of bodies which retain the same form, are permanent in the intermediate temperatures between the freezing and boiling points of water; and we may infer by deduction, that the same law obtains throughout the whole of the scale of heat *."

Admitting that there is no sensible deviation from permanence of capacity in that part of the scale of temperature intermediate between the freezing and boiling points of water, it cannot be inferred, by any strict induction, as Crawford supposes, that the same permanence will continue at all temperatures. It is even far from being improbable, that a change of capacity may arise from changes of temperature, when these are considerable; and if the

* Treatise on Animal Heat, p. 65.

view which I have given of the cause of the difference of capacities in bodies be just, such a change must take place. If the quantity of caloric contained in bodies be in part proportional to their rarity, since increase of temperature is accompanied by expansion, it seems necessarily to follow, that it must give rise to some enlargement of capacity. When the volume of a body is increased, without the direct application of caloric, as in the gases by withdrawing pressure, their capacities are augmented. Is it not, therefore, reasonable to believe, that when the volume is augmented by the operation of caloric itself, there should still be an augmentation of capacity? Indeed, in the former case, the augmentation of volume, and ultimately of capacity, are really owing to the operation of caloric; for the withdrawing pressure only removes an obstacle to its exertion; and the fact therefore, at once proves, that when the volume of a body is enlarged, by the operation of caloric, the capacity is also increased. And as enlargement of volume is a consequence of augmentation of temperature, it seems to follow that it must give rise to enlargement of capacity.

The influence of the specific attraction of bodies to caloric, in determining the capacity, may indeed be greater than that of the volume; but still the other must operate to a certain extent, and this extent it is not possible *a priori* to determine, for we do not know the relative influence of these two causes in giving rise to the specific capacity, and still less do we know the amount of expansion through the whole scale of temperature. This conclusion, too, is not weakened by the fact, admitting it to be established, that the capacities are permanent between the freezing and boiling points of water; for this part of the scale of temperature is so inconsiderable, compared with the whole, that no just inference can be drawn from any fact relating to it, as to what will happen in other parts of the scale; and the degree of expansion which bo-

dies experience in passing through it must be so inconsiderable, compared with their whole expansion, as may be incapable of producing any sensible deviation from the permanence of capacity. But even this is not well ascertained; for there is a source of error in the experiment of Crawford to establish it, in his previously taking for granted, that the mercurial thermometer is an accurate measure of temperature. This latter point is established by the very experiment by which the permanence of capacity is established, and there is in the investigation something approaching to reasoning in a circle. Equal portions of water, at different temperatures, are mingled together, and it is observed whether the mean temperature between the two is indicated by the thermometer. If it be, it is concluded that the expansions of the thermometrical fluid are equable, and of course that they give accurate indications of temperature. But in drawing this inference, it is supposed, that the capacity of the water is permanent; for if it were not, it is possible that the deviation from permanence in the capacity might counterbalance the deviation from equality in the expansions of the thermometric fluid, and of course conceal it. Again, the permanence of capacity is determined by the same experiment, assuming now that the thermometer is an accurate measure of temperature; for if it were not, it is equally obvious, that its irregularities might counteract irregularities in the capacities, and be so adjusted to them as to balance each other, in consequence of which a thermometer put into the mingled portions of fluid should indicate the precise arithmetical mean. Thus, if the expansions of the thermometric fluid proceed in an increasing ratio, the temperature indicated by the thermometer, in the mixture of two equal portions of a liquid at different temperatures, must be below the real mean. If, on the other hand, the capacity of the liquid increases as its temperature rises, the resulting temperature would be above the mean. Now, it is possible,

that both these conditions may be present, and modify each other. The experiment therefore is indecisive; and it is still more doubtful, when there is not merely the possibility of this, but when it is actually probable *a priori*, both that the expansions of the thermometer proceed in an increasing ratio as the temperature rises, and that the capacities likewise increase, whence such an adjustment may be established to the extent required.

Dr Crawford, sensible of this, endeavoured to establish the regularity of the mercurial thermometer in another manner, not implying any thing as to the permanence of capacity. The experiment has been stated, (p. 220.) as well as the conclusion drawn from it, that the mercurial thermometer is very nearly an accurate measure of temperature. But Crawford perhaps rather under-rated the increasing expansions of mercury: the thermometer does not approach so nearly to accuracy as he supposed; and the experiment by which he determined the permanence of capacity in water between 32° and 212° , is not perfectly conclusive. The probabilities still continue in favour of the conclusion, that in common with all bodies, it suffers an increase of capacity with augmentation of temperature.

That this is the case with regard to some bodies, has even been ascertained. Gadolin observed it in lintseed oil; and Crawford discovered it in some saline solutions, and in a mixture of sulphuric acid and water, and of alkohol and water, by finding, that when the constituent parts of these solutions or mixtures were mixed at a high temperature, they produced less sensible heat than when mixed at a low temperature; the compound, in the former case, being capable of containing more caloric than in the latter: he also found, by direct experiment, that mixing together equal parts of diluted sulphuric acid at different temperatures, the resulting temperature was greater than the arithmetical mean*. Now, if even in the small part

* Treatise on Animal Heat, p. 479.

of the scale of temperature at which we can make our experiments, there are perceptible deviations from uniformity, much more is it probable, that in the whole extent of the scale they will happen, and to an extent of which we can know nothing. These variations arise probably from the expansion produced by caloric itself, by which the volume of the body is altered, and the law by which the quantity of caloric it contains at a given temperature is modified. But we know nothing of the total amount of expansion in bodies from the real zero, and therefore, if expansion enlarge capacity, as it probably does, it must be difficult or impossible to say what the amount of this enlargement is; of course, what may be the difference between the capacity of a body, estimated at the temperature at which we can subject it to experiment, and its capacity at lower points in the thermometrical scale.

FROM the operation of the general law now illustrated, with regard to the distribution of caloric in bodies, may be explained its extrication in many cases of chemical action, and its absorption in others. Dr Irvine first perceived its importance in this point of view. Having shewn the insufficiency of the vague hypotheses on which the production of heat and cold from chemical mixtures had been attempted to be explained, particularly of the hypothesis of Newton, that the heat produced in the mutual action of bodies is owing to the violent motions and collisions of their particles, he observes, “that the reason why heat is produced by mixing fluids seems to be, that the ingredients which compose the mixed fluid are in a different state with regard to heat from what they were before: it would seem, that whatever is the cause of heat, it has a greater effect in heating the bodies after the mixture than it ought to have had in proportion to its power of heating the ingredients before mixture *.” In other words, in such

* Chemical Essays, p. 177.

mixtures the capacity of the compound for caloric is inferior to the mean of the capacities of the substances combined, and hence an augmentation of temperature must take place. This principle he illustrated, and also established by experiment. It was successfully applied by Dr Crawford to explain the heat which is produced in combustion, and other chemical processes, as well as the heat generated by respiration in the animal system. On the other hand, when the capacity is enlarged, or that of the compound is greater than the mean capacity of its constituent parts, an absorption of caloric must follow; and on this principle is explained the cold attending some combinations, as the solutions of salts in water, and the intense colds generated by what are named Freezing Mixtures. The proposition is indeed probably just, that all variations of temperature, not arising from the immediate communication of caloric from an external source, originate in changes of capacity. That they do arise from this cause in many cases can be experimentally established, and any exceptions to the proposition are doubtful or imperfectly understood.

SECT. V.—*Of the quantities of Caloric which different forms of the same bodies contain.*

HAVING illustrated the law, that different bodies, at the same temperature, contain different quantities of caloric, in proportions regulated neither by their weights nor volumes, I have next to observe, that a similar law exists with regard to *different forms* of the same body; that a body in the liquid form contains more caloric, or requires a larger quantity to produce a given change of temperature in it, than it does while solid; and in the state of air or vapour,

it contains still more than it does in the liquid form. Hence, when a solid is melted, or a liquid is converted into vapour, quantities of caloric are absorbed, which have no effect in producing augmentation of temperature. This phenomenon, constituting what has been named Latent Heat or Latent Caloric, probably depends on change of capacity, though it has also been referred to a different cause. It is necessary to state first the facts by which it is established; the opinions with regard to it may then be considered.

The fact of the absorption of caloric in these changes of form was discovered by Dr Black. Previous to the year 1762, he had described in his lectures some of the experiments by which it is established. Wilcke, in 1772, read to the Academy of Sciences at Stockholm, a dissertation, in which he states, as his own discovery, the fact that ice in melting absorbs a quantity of caloric; and there is no evidence that he was informed of the discoveries of Black. The imperfect observations and loose conjectures of De Luc on the same subject cannot be regarded as establishing any claim to the discovery; nor has it with more justice been assigned to Lavoisier, who, however, can scarcely be acquitted from the charge of having sought to appropriate it, with regard to æriform fluids, with slight modifications, without sufficient acknowledgment to Dr Black.

The truth of the fact is apparent, when the phenomena attending liquefaction or vaporisation are attentively examined, and it was the observation of these that led Dr Black to the discovery. If ice, for example, be at a temperature below 32° , on exposing it to a warmer atmosphere, it receives caloric, and gradually rises to that point of the thermometrical scale. But the moment it reaches it, the rise ceases; it begins to melt; melts slowly; and during the whole time of melting, its temperature, as well as that of the water flowing from it, are stationary at 32° . Yet caloric continues to be communicated as before; and

that this caloric is absorbed by it, Dr Black remarked, is obvious, from the atmosphere being cooled by the melting ice, and a current of cold air descending from the vessel the whole time. Here, therefore, a quantity of caloric is absorbed, or disappears during the fusion, without raising the temperature. The same phenomenon is observed when a liquid is converted into vapour. If we take a portion of water and communicate caloric to it, its temperature is raised, and this rise proceeds while the caloric is added, until, under the common atmospheric pressure, it arrives at 212° of Fahrenheit. At this point it begins to boil, or to be converted rapidly into vapour, which escapes. But while it is suffering this change, its temperature is stationary, as is that also of the vapour arising from it, a thermometer in either indicating 212° . The conclusion is in this case the same as in the other. The vessel containing the water placed on a fire must continue to receive caloric after it boils as it did before; but the caloric thus added is absorbed without producing augmentation of temperature. The liquid in the one case, and the vapour in the other, after it is formed, has its temperature raised by increments of heat.

Dr Black, not satisfied with the general observation of these phenomena, endeavoured to ascertain the fact with more accuracy, and to discover even the quantity of caloric which disappears.

In two glass vessels of the same size and weight, he put portions of water,—five ounces in each. The water in one of the vessels he froze by a freezing mixture, and removing the vessel into an atmosphere at 47° , allowed the ice in it to rise to the temperature of 32° . While this was doing, he cooled the water in the other vessel without freezing any of it, to 35° , and placed in it a delicate thermometer. It was exposed to the same atmosphere at the temperature of 47° as the other, and the rise of its temperature observed by the thermometer. At the end of

half an hour it had risen 7 degrees. The ice in the other vessel was not melted; its temperature remained at 32° , though it must have received caloric from the surrounding atmosphere equally with the other. It continued to melt slowly; at the end of $10\frac{1}{2}$ hours a very small piece of it only remained unmelted; in a few minutes more, this was melted; and, on introducing a thermometer into the water, its temperature was 40° ; this rise, while in contact with the ice, being owing to its imperfect conducting power.

From this experiment, he remarked, it appears, that exposure to an atmosphere of 47° for 21 half hours was requisite to melt five ounces of ice, and raise the temperature of the water produced from it to 40° . Now, the quantity of heat which it had received during this time may be estimated from the quantity communicated to the water in the other vessel, and discovered in it by the rise of temperature it produced; for as the two vessels were in situations perfectly alike, the same quantity must have been communicated to each. In half an hour, as much heat had been communicated to the water as raised its temperature 7 degrees. In 21 half hours, therefore, the quantity communicated to the ice, and absorbed by it, must have been 7×21 , or such as would have raised the temperature of the same weight of water 147 degrees. Yet no part of this appeared in the ice-water, except 8 degrees, the temperature of that water at the end of the experiment being only 40° : the remaining 139 degrees must have been absorbed, therefore, by the ice in melting, without occasioning any rise of temperature.

A quantity of ice, weighing $59\frac{1}{2}$ drachms, at 32° , was put into a quantity of water, weighing $67\frac{1}{2}$ drachms at the temperature of 190 degrees. In a few seconds the ice was melted, and the temperature of the resulting fluid was 53° . In this experiment, the temperature of the water was reduced from 190° to 53° ; the vessel in which this warm

water was contained, and which must have been also at 190° , was likewise reduced to 53° ; this vessel weighed 8 drachms; but it being ascertained by experiment that its power in heating bodies was not more than half that of water, the 8 drachms may be regarded as equivalent to 4 of water. A quantity of water, therefore, weighing $67\frac{1}{2}$ drachms, and a quantity of matter having the same heating power, amounting to 4 drachms, had their temperature reduced from 190° to 53° , or lost 137 degrees. These were communicated to the $59\frac{1}{2}$ drachms of ice at 32° ; and according to the relative proportions of the hot and cold matter, if there had been no loss, ought to have raised the ice 86 degrees; but they produced a rise of only 21 degrees. Here, therefore, 65 degrees disappeared,—a quantity which would have been sufficient to raise the temperature of a quantity of water equal in weight to the ice, 143 degrees. This quantity of heat, however, had entirely disappeared, and so far this experiment corresponds nearly with the former. Dr Black confirmed both by a very simple experiment, adding a given weight of ice at 32° to the same weight of water at 176° ; the ice was melted, and the temperature of the whole liquid was still not more than 32° *.

In the conversion of bodies from the liquid to the aëri-form state, a similar absorption of caloric takes place without raising the temperature either of the vapour or of the body suffering the change. This likewise Dr Black established by experiment.

In several cylindrical tin-plate vessels, placed on an iron-plate, heated by a fire beneath, equal portions of water were put, at the temperature of 50° . After 4 minutes the water began to boil, and in 20 minutes was entirely dissipated. In 4 minutes, therefore, these portions of water had been raised from 50° to 212° , and of course had

* Black's Lectures, vol. i, p. 121—4, 5.

received a quantity of heat capable of raising the temperature of that liquid 162 degrees, or at the rate of $40\frac{1}{2}^{\circ}$ each minute. After the boiling commenced, heat must have been communicated from the hot iron-plate to the liquid as before; in the 20 minutes, therefore, 810 degrees must have been absorbed. Yet these were not discoverable by any rise of temperature, the boiling liquid and the vapour arising from it being constantly at 212° *.

This result was confirmed by another experiment more striking. A quantity of water was put into a strong phial, so as to fill it about one-half. It was corked strongly, placed in sand, and heat applied. It began to boil, but in a short time this ebullition ceased; the pressure on the water, from the accumulation of the vapour, being sufficient to prevent it; the fluid, therefore, had its temperature soon raised above 212° . It rose to 222° . The cork was then suddenly withdrawn. But instead of the whole water rushing out in vapour, as might have been expected, from its being heated 10 degrees above the temperature at which it passes into that state, only a small part of it escaped, and the remaining quantity fell to the temperature of 212° ; the quantity of vapour which was formed absorbing the whole excess of heat above that point.

The experiment was repeated by Mr Watt on a large scale. In a copper digester, with a valve, he heated a quantity of water, and when it began to boil, closing the valve, he allowed it to remain on the fire half an hour. Removing it, and opening the valve, a quantity of vapour rushed out with great force; but instead of the whole of the water having passed into vapour, as might have been expected, considering the high temperature to which it must have been raised, he found, that of three inches, only one inch had escaped under this form †.

* Black's Lectures, vol. i, p. 158.

† Ibid. p. 159, 160.

This experiment illustrates the phenomena attending the conversion of a liquid into vapour. Under the ordinary pressure of the atmosphere, water cannot be heated beyond 212° , since, as soon as it arrives at this, vapour is formed, and this absorbing caloric, prevents the temperature from rising, and in some measure conceals the real quantity received. But by confining it under a greater pressure, the early formation of vapour is prevented, and when the pressure is removed, the quantity of caloric which disappears is more clearly perceived.

Dr Black remarked, that the same fact is established by the reduction of temperature which attends the transition of a body into vapour *in vacuo*. The temperature of hot water, for example, in the vacuum of the air-pump, will fall rapidly to the 90th, or even to the 70th degree of Fahrenheit. This is shewn still more remarkably in the evaporation of certain volatile fluids, as alcohol or ether,—a considerable degree of cold always attending it. This was first accurately observed by Dr Cullen. On wetting the bulb of a thermometer with either of these liquids, and suspending it in the air, he observed, that the mercury in the thermometer sunk rapidly. The more volatile the liquid was, the greater was the reduction of temperature, and whatever hastened the evaporation, as directing a current of air on the wet bulb, increased the cold. By causing a rapid evaporation of ether in the air-pump, such a degree of cold was even produced, as to freeze a portion of water in a vessel in which the phial containing the ether stood *. The explanation of these experiments is obvious. These fluids are so volatile as to evaporate at the common temperature of the atmosphere; and in passing from the liquid to the æriform state, they follow the general law, and absorb caloric from the matter with which they are in contact.

* Black's Lectures, vol. i, p. 162.

Lastly, if a substance be disengaged from a combination, and passes into the aëriform state, the chemical action by which it is disengaged is attended with a less production of heat than when a similar action is excited, without the disengagement of an aëriform fluid, as was shewn by Lavoisier, by several experiments*.

All these facts prove the truth of the general law, That *When bodies pass from the solid to the liquid, or from the liquid to the aërial form, a quantity of caloric is absorbed, which has no effect in raising the temperature of the liquid, or of the vapour or air which is formed.*

It may be expected, that the quantity of heat absorbed will be disengaged and rendered sensible, when the body returns to its former state. This accordingly happens. When a liquid is exposed to an atmosphere colder than what would be sufficient to freeze it, its temperature is gradually reduced, until it arrives at the point at which it congeals. But whenever it attains this, its temperature becomes stationary, and continues so until it has become entirely solid, although the cold atmosphere must be abstracting caloric from it as before.

To render this more evident, Dr Black exposed a quantity of pure water, and another equal quantity of water to which a little salt had been added to prevent it from freezing, in similar vessels, to an atmosphere below 32° . Both were soon cooled down to this point. The water in which the salt was dissolved continued to descend still lower in its temperature: but the pure water, beginning to freeze, remained stationary at 32° ; the heat which it had absorbed, when it passed from the state of ice to that of water, being now given out as it returned to the state of ice; and this keeping up its temperature, though the cold atmosphere must have been acting on it equally as on the other.

There is another experiment in which this evolution of

* Mémoires de l'Acad. des Sciences, 1777, p. 430.

caloric is rendered apparent. If agitation be avoided, water can be cooled a number of degrees below its common freezing point, or 32° , without freezing. But if it be then agitated, ice is instantly formed, and the temperature rises to 32° . This arises from the evolution of the portion of latent heat contained in the quantity of water that freezes*; the quantity evolved being of course greater, as, from the previous greater cooling, more of the water is converted into ice.

A similar extrication of heat attends the reduction of a vapour or gas to the liquid form. If a certain weight of aqueous vapour be condensed, by receiving it in water, the water will have its temperature raised much higher, than by the addition of the same weight of water at the same temperature as that of the vapour. This was observed by Dr Black, and, with the assistance of Dr Irvine, he made several experiments to discover the quantity of heat evolved. It was difficult to guard against the abstraction of caloric, by the vessels and the surrounding air; but in general it was concluded, that the quantity was not less than 774 degrees†. Mr Watt, in repeating the experiments, supposed it to be 825° , and from others he has fixed it at not less than 900° , and not more than 950 degrees of Fahrenheit's scale.

Mr Watt ascertained this too in another mode,—condensing the steam by mechanical pressure. He fitted a piston accurately to a metallic cylinder, and transmitting watery vapour through it, to expel the atmospheric air, when the cavity of the cylinder was filled with vapour, he pushed down the piston, so as suddenly to condense it, the caloric evolved being communicated to water in which the extremity of the cylinder had been put. The quantity of heat thus extricated, according to Dr Crawford's state-

* Black's Lectures, vol. i, p. 128.

† Ibid. p. 172.

ment, was such as would be sufficient to raise the temperature of an equal weight of a body having the same capacity as water, and which would not evaporate, 943 degrees of Fahrenheit's scale. Yet, previous to the condensation, the cylinder with the contained vapour were only at the temperature of 212° .

Such are the facts and experiments by which Dr Black established the general truth,—That when bodies pass from the solid to the liquid, or from the liquid to the aëriform state, they absorb a quantity of caloric which does not raise their temperature, and which is again evolved by them, when they return to their former state. The whole investigation is a model of physical research; the discovery, unlike many others, was suggested by no prior train of speculation, but was separated, as has justly been observed, by a vast interval from the previous steps of our knowledge; and it was left in no respect imperfect, but was established by its author, on evidence which it is impossible to controvert, and to which the progress of the science has made no addition. To Dr Black is due the honour of having established the two principal laws yet known with regard to caloric,—that it is contained in bodies at the same temperature in specific quantities, and that it is absorbed, without producing augmentation of temperature, when bodies pass to the liquid or aëriform states,—laws which form the basis of much of the modern system of chemistry.

The portion of caloric, or of Heat, thus absorbed in fluidity or vaporization, appearing to lose its properties, having no effect in raising temperature, and its existence being no otherwise known than from observing its absorption at the formation of the fluid or vapour, or its evolution on the reduction to the liquid or solid state, Dr Black named Latent, to distinguish it from that which is discovered by the thermometer, and which, in opposition to the other, he termed Sensible. The term Latent is convenient, as denoting briefly the portion of caloric absorb-

ed or evolved in these changes of form, though there is probably no foundation for supposing its properties to be lost, nor any just reason for distinguishing it as it exists in bodies, from the rest of the caloric which they contain.

In establishing the doctrine of latent heat, Dr Black's experiments were confined to water in its different states. There could be no doubt, however, but that the same law is observed by other bodies in their changes of form. This has been ascertained by other chemists, and the quantities of caloric absorbed during these changes determined. Dr Irvine found, that spermaceti, in melting, absorbs a quantity of heat, which would be sufficient to raise the temperature of liquid spermaceti 145 degrees; wax, a quantity which would raise its temperature in the fluid state, 175 degrees; and tin, a quantity equal to what would elevate its temperature in the solid state 500 degrees. Willeke states the heat absorbed by ice in melting, as less than that Dr Black gives. According to the average result of Dr Black's experiments, it is equal to what would raise the temperature of water 140 degrees. Willeke makes it equal only to 129°. Lavoisier and Laplace fix it at the medium nearly, or 135° of Fahrenheit; Cavendish gives also this number as established by his own experiments, while Gadolin makes it 143°;—differences which may arise from the difficulties attending the experiment, or, as Mr Dalton has suggested, from the capacity of water being perhaps different at different temperatures, so that in melting ice by water at different temperatures, unequal quantities of caloric will appear to have been taken from it. Landriani found, that sulphur, alum, borax, and other salts, as well as some metallic compositions, when they pass into a solid state, from a state of fusion, obey the general law, and evolve heat*. Hassenfratz, on freezing quicksilver, ascertained, that in melting it absorbs as much heat as would raise the temperature of liquid mer-

* Journal de Physique, t. xxvi, p. 88.

cury 152 degrees of Fahrenheit's scale*. Lastly, Dr Irvine *junior* prosecuted his father's experiments, and determined the quantities of caloric absorbed in the liquefaction of the following bodies. In the liquefaction of bismuth, as much was absorbed as would have raised the temperature of the bismuth in its solid state 475° of Fahrenheit's scale; in that of tin 507°; of zinc 493; of lead 150°; and of sulphur 143°. From these experiments we do not discover, as he remarked, "any ratio by which the quantity of caloric, absorbed in liquefaction, seems to be guided; it obviously does not increase with the difficulty of fusion, but most probably has some connection with the relative capacity of each body in its solid and fluid state†."

The following table exhibits the results of the experiments on this subject, the latent heat of each substance being measured by the capacity of the solid, instead of by that of the liquid, which in the greater number of cases it is more difficult to determine; with the exception of spermaceti and wax, and also of quicksilver, in which, from the difficulty of ascertaining, the capacity of the solid, the latent heat is necessarily referred to that of the fluid. The basis of the table is taken from the Essay on Latent Heat, by Dr Irvine *jun.* already referred to.

	Melting point.	Latent heat.	Authority.
Ice, -	32	155.5	Black.
— -	—	150	Lavoisier.
— -	—	143.3	Wilcke.
Spermaceti,	113	145	Irvine <i>sen.</i>
Bees wax,	142	175	—
Tin, -	442	500	— <i>jun.</i>
Bismuth, -	476	550	—
Lead, -	594	162	—
Zinc, -	700	493	—
Sulphur, -	226	143.6	—
Quicksilver,	—40	152	Hassenfratz.

Journal Polytechnique, t. i, p. 128.

† Nicholson's Journal, vol. ix, p. 52.

From this change in the distribution of caloric, which takes place when bodies change their forms, many chemical and natural phenomena are explained.

The absorption of heat, accompanying the change from the solid to the liquid form, explains the fixity of the point in the thermometrical scale at which bodies melt. Ice melts at 32° of Fahrenheit, and whenever any mass of ice is heated to that temperature, the farther communication of heat, however rapid, has no effect in raising its temperature, till the whole is converted into water; since, as quickly as the ice is melted by the caloric, as quickly is a portion of it absorbed by the fluid formed. This is exemplified in the long time before large masses of ice, or collections of snow, are melted by a thaw. Were it not for this absorption of heat, the liquefaction of masses of ice and snow, in the colder climates, at the approach of spring, would take place almost instantaneously, when the temperature of the atmosphere rose above 32° ; whereas, from this circumstance, it is gradual and progressive, by which the water formed is distributed more slowly, and the too sudden rise of temperature, which would prove fatal to vegetables, is prevented.

The reverse of this, or the extrication of heat, when water is converted into ice, is equally beneficial; since, were it otherwise, the freezing of large collections of water would be extremely rapid, whenever the temperature of the atmosphere was at or below 32° . But from this extrication, the freezing is gradual, and, at the same time, a large quantity of heat is given out by the water in passing to the solid state, by which the approaching cold is moderated, and the congelation rendered more slow.

Similar general effects arise from the operation of this law in vaporisation. When the earth is much heated by the sun's rays, water is evaporated from its surface, and from rivers and the ocean, and the conversion of this into vapour is necessarily accompanied with the absorption of

caloric. Hence evaporation is the most powerful agent employed by nature to moderate excessive heat. On the contrary, when the vapour of the atmosphere is condensed by cold, and descends in rain or snow, it gives out the caloric it had received, which is then beneficial rather than hurtful. Much of this vapour must even be wafted from the torrid zone, where evaporation must be most rapid, towards the polar regions; and being condensed in its progress, in colder climates, will prove a source of heat.

The process of artificial refrigeration is explained on the same principle. By allowing water to filtrate slowly through porous earthen vessels, so as to present an extensive humid surface to the atmosphere, it passes rapidly into vapour, and in this vaporisation absorbs so much caloric as to produce considerable cold. Liquors are cooled, and in warm climates ice is formed, by arrangements of this kind, and this even when the temperature of the atmosphere is several degrees above 32° *. This artificial formation of ice is carried on in Bengal to a considerable extent. The cold from the evaporation is no doubt considerably accelerated by the rapidity of that process from the dryness of the atmosphere, and hence, in a humid atmosphere, the process would not succeed at a similar average temperature. A considerable part of the effect too depends, as Dr Wells has shewn, on radiation from the surface of the water, and hence the success is always greatest in nights which are calm and serene *.

The theory of freezing mixtures is deduced from the doctrine of latent caloric. These are mixtures of saline substances, which, at the common temperature, by their mutual chemical action, pass rapidly into the fluid form, or are capable of being rapidly dissolved in water, and by

* Philosophical Transactions, 1793, p. 56.

† Wells on Dew, p. 129.

his quick transition to fluidity, absorb caloric, and produce degrees of cold more or less intense.

In other cases of chemical action, substances pass from the gaseous to the fluid, or from the fluid to the solid form, and the rise of temperature which attends these transitions is referred to the evolution of latent caloric, which must be their result.

The use of steam, as a vehicle and source of heat, affords an example of the scientific application of these principles. By conveying steam into water, it is condensed, and by the evolution of the latent heat by the condensation, the temperature of the water is raised, so as soon to arrive at 212° . In certain arts, as in that of dyeing, where large quantities of water are to be heated in separate vessels, this method has superior advantages. By having a common boiler, from which the vapour is conveyed by tubes, the loss of heat is less than if fire was applied to each vessel, and the vessels are subject to less wear, and may be constructed at less expence. This method has accordingly been employed with success*. Another application of the same principle is that of heating rooms by conveying steam through tubes, proposed in an early volume of the *Philosophical Transactions*, and since revived. The steam in its progress is condensed gradually, and gives out its latent heat, so as to produce an equable warmth. A well-constructed apparatus for this purpose has been described by Mr Snodgras, by whom it was applied with success to the heating of cotton-mills†. Mr Buchanan has, in a separate publication, given more minute details on this subject, which may be consulted with advantage‡. For this and similar purposes steam is well adapted, as it has the advantage of being free from any danger of fire, the

* *Philosophical Magazine*, vol. x. p. 46.

† *Ibid.* vol. xxvii, p. 172.

‡ *Essays on the Economy of Fuel.*

boiler whence the steam is brought being erected without the building; and there is also a saving of fuel. There is a considerable expence, however, in erecting the apparatus, on which account, and also as being more easily managed, the mode of heating apartments, by the introduction of warm air, may in particular situations be preferred. The mode of applying heat from the condensation of steam, has been proposed to be applied to the drying of gunpowder, as attended with less risk than the common mode.

The modern improvements in the Steam-engine, as they originated from Dr Black's discovery, so they afford the most important practical application of the doctrine of latent heat. In the engine wrought previous to the improvements of Mr Watt, the steam was received into a cylinder, to which a piston was adapted; the piston by the weight attached to its arm being elevated to the top of the cylinder, and the cavity beneath filled with steam. This was condensed by a jet of cold water, and the piston was of course forced down by the pressure of the atmosphere. To raise this, steam was again introduced from beneath, and thus the alternate elevation and depression of the piston were effected. But in this way, it is obvious, that there was an immense waste of heat, and this altogether concealed, while the facts relating to latent caloric were unknown. By the jet of cold water, not only is the steam condensed, but the cylinder is cooled, as it is also by the entrance of the atmospheric air. When, therefore, the steam from beneath is again introduced, a great part of it must be condensed and lost, by its heat being abstracted by the cold cylinder and piston, and its elasticity cannot operate with effect until the whole is again elevated to 212° . At each stroke of the engine this waste is repeated, and thus, according to Mr Watt's calculation, at least half of the steam produced in the boiler is lost.

Mr Watt's principal improvements consisted, 1st, in condensing the steam, not in the cylinder, but in a vessel

communicating with it by a pipe with a valve, which being exhausted of air, the steam rushes into it when the communication is opened, and is condensed by the vessel being kept cold by immersion in water; and, 2dly, by excluding from the cylinder the atmospheric air, and depressing the piston by steam introduced above it, and condensed in the condensing vessel alternately with the steam beneath. Thus, the whole may be kept at the temperature of 212° , and the waste of heat in the old method obviated. Dr Black justly characterises the engine in this state as the master-piece of human skill, and no less justly observes, that it has not been "the production of a chance observation, but the result of deep thought and reflection, and really a present by philosophy to the arts."

HAVING stated the phenomena and applications of latent heat, it remains to consider the opinions that have been advanced with regard to its cause. It has been considered under very different points of view; some philosophers having supposed the absorption of caloric that attends liquefaction and vaporisation to be the cause of these changes, others regarding it as the effect.

By Dr Black the first of these opinions was maintained. "I consider," says he, "fluidity as depending immediately and inseparably on a certain quantity of the matter of heat which is combined with the fluid body in a particular manner, so as not to be communicable to a thermometer or to other bodies, but capable of being extricated again by other methods, and of reassuming the form of moveable or communicable heat *." He applied the same theory to vaporisation. "When a fluid body is raised to its boiling temperature by the continual and copious application of heat, its particles suddenly attract to themselves a great quantity of heat, and by this combina-

* Black's Lectures, vol. i, p. 144.

tion their mutual relation is so changed that they no longer attract each other, but avoid each other, separating to at least ten times their former distance, and would separate much farther were they not compressed by the weight of the atmosphere; and, in short, they now compose a fluid, elastic and expansive like air. This new form of aggregation is the effect of a new combination of heat with the primary particles of water, and is a sufficient indication of this union, in the same manner as fluidity was a sufficient mark of a sudden and copious combination of heat with the particles of ice *."

In this theory, then, the absorption of caloric in liquefaction and vaporisation is considered as the cause of these changes of form, and the latent heat existing in a fluid or vapour is that which preserves it in these states. Dr Black, though he did not state the opinion fully, appeared inclined to suppose these changes analogous to chemical combination, to regard the caloric which disappears as entering into union with the body fused or evaporated, and owing to this combination its loss of properties. He considered, says Professor Robison, latent heat "as *united* with the substance of the body in a way very much resembling many chemical combinations;" and as "producing those new modes of aggregation by a true chemical combination with the particles of the body †." This opinion was expressed with less hesitation by other chemists, as by De Luc ‡ and Seguin §, and is still not unfrequently maintained.

Dr Irvine viewed these phenomena under a very different light. He considered them as arising from changes of capacity accompanying the changes of form. Temperature depends not merely on the action of caloric, but

* Black's Lectures, vol. i, p. 175.

† Ibid. p. 514.

‡ Idées sur la Météorologie.

§ Annales de Chimie, tom. iii, p. 193.

on this modified by that peculiar relation of bodies to caloric which we denominate capacity. If the capacity of a body be enlarged, the quantity of heat communicated to it remaining the same, its temperature must fall; if the capacity be diminished under the same condition its temperature must rise; or if the capacity be enlarged, while heat is proportionally communicated, this heat will be absorbed by the body, and remain in it without any increase of temperature. If, therefore, in fusion and vaporisation, an augmentation of capacity takes place, a quantity of caloric must be absorbed proportioned to this augmentation, which can occasion no augmentation of temperature: when the body is reduced to its former state, its capacity for caloric being diminished, this quantity must be again given out; and in either case the temperature must continue stationary while the change is going on. These changes, accordingly, Dr Irvine supposed to be produced, and to be the cause of the phenomenon of latent heat. This view of the subject is thus stated: "The reason why a body cannot be heated while it is melting is, that it is then changing its capacity. From a substance that was easily heated, it changes to one that is heated with difficulty. All bodies in a fluid state seem to be heated with more difficulty than when in a solid state. Not that a body in a fluid state transmits heat more slowly than when the same body is in a solid state. On the contrary, it transmits heat better in a fluid than in a solid state. But the same quantity of heat applied to the same body in a solid form, and in a fluid state, will heat the solid a greater number of degrees than it will the fluid *." In other words, the fluid becomes a body capable of containing more caloric at a given temperature than the solid: hence at the moment of change it must absorb a quantity of caloric without any rise of temperature. On this view it is obvious, that there is no reason to suppose that the calo-

* Irvine's Essays, p. 52.

ric absorbed during liquefaction and vaporisation loses its properties, or passes into any peculiar state of combination : it goes to sustain the existing temperature according to the augmented capacity : it has been absorbed without raising temperature, because the capacity of the body has been enlarged ; and when the capacity is diminished in the reverse change of form, it is of course evolved. A body in one form, in a word, contains more caloric than in another form at the same temperature, exactly as one body contains more than another does : or, according to this theory, the cause why water contains a quantity of caloric above that in ice at 32° , is the same as that by which water contains a quantity of caloric above that which quicksilver contains ; and were it possible to convert quicksilver into water by a process similar to that by which we convert ice into water, we should have the phenomena of latent heat.

This question presents rather an interesting subject of discussion ; and it is more necessary to consider it somewhat in detail, as the theory of Irvine, which gives the just explanation of the phenomena, has been much misunderstood.

It is obvious, that the change of form, and the evolution or absorption of caloric being, to our observation, simultaneous, we have no direct means of discovering which precedes the other. We must therefore seek to determine the merits of these opinions on other grounds.

If we regard them as hypotheses, that of Irvine is more simple than the other, and more analogons to the relations of caloric to matter. It is obvious *à priori*, that at some stage in the scale of temperature, the changes of fluidity and vaporisation must take place from the operation of the expansive energy of caloric. In such changes there is an alteration in the mechanical state of the body ; and as the capacities of bodies for heat are obviously connected with their mechanical state, nothing can be more probable, than

that a change of capacity must attend the change of form. We know nothing of the properties of caloric in an insulated state, but merely its effects on matter; and no reason can be stated in support of the proposition, that these effects shall be the same on bodies of different kinds, or in different states. If a solid body have a certain relation to caloric; suffer from it a certain degree of expansion; conduct it, after a certain ratio; or require a certain quantity to produce a given temperature; when it is converted to the fluid or aëriform state, we have no reason to expect that its relations to caloric should be the same as they were in the solid state. We find in reality that they are changed; the body in its new state suffers a different degree of expansion; its conducting power is also no longer the same; and we may equally presume that its capacity for caloric will be changed.

Nothing also can be more certain, than that if such a change do happen, the augmentation of temperature will observe a different law from what it did while the body was in its former state. If by fusion, or vaporisation, the capacity of a body be enlarged, either its temperature must fall, or a quantity of caloric must be absorbed, by which no augmentation of temperature will be produced. The first cannot happen; for in this case the temperature of the body falling below its fusing or evaporating point, the change of form cannot proceed; the second event, therefore, must be that which will occur; in other words, if by applying heat, we raise and preserve the temperature sufficiently high to cause the change of form to proceed, then if this change of form be accompanied by an increase of capacity, the heat applied must be absorbed, and must become latent, or occasion no increase of temperature. The quantity absorbed will be in proportion to the capacity of the body in the new form; that is, it will require as much caloric as is requisite to keep up its temperature according

to that capacity, from the point of privation in the thermometrical scale, to the point at which it has assumed the new form ; and there is no fact which shews that the quantity really absorbed is not in proportion to this. The phenomena, therefore, attending fusion and vaporisation, are precisely those which must occur, if these changes are accompanied by an enlargement of capacity.

The opposite opinion, considering it also as an hypothesis, is much less perfect. We have no proof that caloric is capable of entering into bodies in more intimate combination than that which constitutes temperature : even if it did, we perceive no cause why, at a certain stage of the thermometrical scale, bodies should combine intimately with caloric, which they did not before do ; and why, after another interval in the thermometrical scale, this combination should be renewed. Nor does it appear how, in a combination so intimate as to be able to suppress entirely the properties of caloric, the properties of the body combining with it are not also changed. Neither are the phenomena attending these changes of form analogous to those of chemical combination. Although at first view a portion of caloric appears to lose its properties since it is absorbed without causing any rise of temperature, a more enlarged consideration of the subject shews, that this is no necessary conclusion, as the same results must happen if an augmentation of capacity takes place. The temperature of a body depends on its capacity, and the quantity of caloric it contains : if the capacity be increased, a quantity of caloric proportional to this must be absorbed, to keep up the existing temperature ; but it loses none of its properties, nor passes into any state different from the rest of the caloric which the body contains. The circumstance, therefore, of the caloric absorbed not producing rise of temperature, is no proof of its having entered into any peculiar combination, since this would equally happen from an augmentation of capacity. The one cause may

indeed *hypothetically* be assigned as well as the other; yet, even as an hypothesis, the latter is superior to the former, since it brings an insulated phenomenon under a general law; and if experimentally established, its superiority is unequivocally demonstrated.

The investigation of this engaged the attention of Dr Irvine for a number of years, and he made a great number of experiments to ascertain the fact. To do so with accuracy is very difficult, for in comparing the capacity of a body in the solid, and in the liquid state, it is necessary that, in the progress of the experiment, it should not change its form; that in determining its capacity in the solid state, it should remain solid; and in determining it in the fluid form, it should continue fluid. This can only be done by the intervention of a third substance, and even with this it is difficult to obtain a range of temperature sufficiently extensive, within which the experiment can be executed on the body in its two states. Dr Irvine's experiments were in a great measure confined to ice and water, operating on the ice when the temperature of the air was below 32° , and on water at temperatures above 32° . He "found the capacities of some suitable bodies, as river-sand or iron-filings, and compared them with that of water in the usual manner. This being done, he used the same body to examine the capacity of pounded ice formed from distilled water or of snow. The temperature of the room and vessel was, in his experiments, always either 32° or below it; most commonly considerably under 32° . He then took a known weight of snow or ice of a known temperature, in a vessel of which the capacity was determined by experiment. Upon this he poured a certain quantity of river-sand washed, or iron-filings of a certain temperature, with as much rapidity as possible. The new temperature was observed after stirring, and allowance was made for the heat gained or lost: the temperature of the mixture was frequently 19° , 20° , 25° , 16° , &c. So

that in a room where the air was below the freezing point, the accuracy of the result could not be affected by the formation of any water ; still there are many sources of inaccuracy remaining. But in Dr Irvine's hands, the capacity of ice always turned out to be less than that of water. In all his experiments, which were very numerous, and repeated with care for many succeeding years, he arrived at results approximating to each other, and concluded, to use his own words, that from the mean of all his trials, the capacity or relative heat of water to that of ice is not in a ratio greater than 5 to 4 or 10 to 8. In like manner, he extended his theory to all other bodies, and in some cases determined, and in all inferred, that it is a general law of nature that the capacity of all solids for heat is increased by fusion, and that of all fluids by vaporisation *." A similar augmentation of capacity, Dr Crawford found, to take place when water is converted into vapour.

The principle of the theory is therefore proved ; and the important fact established, that the change in the relation of the body to caloric is not confined, as Dr Black imagined, to the moment of the change of form ; but that in every subsequent elevation of temperature, the liquid requires more caloric than the solid would have done, and the vapour more than the liquid ; that its capacity, therefore, is increased when it passes from the solid to the fluid, or from the fluid to the æriform state. These experiments, it is important to remark, Dr Black never attempted to invalidate, nor did he attempt to shew by experiment that the reverse was the case. They are therefore decisive of the question.

The augmentation of capacity, it has been said, is not proved to be proportional to the quantity of caloric absorbed, and therefore, besides the portion which the augmented capacity demands, another quantity may, it is sup-

* Chemical Essays, p. 55.

posed, enter into chemical union. This, indeed, cannot be ascertained by direct experiment; for to do so it would be necessary to know the absolute quantity of caloric in bodies, whence we might discover whether the quantity absorbed in these changes of form corresponds with the changes of capacity, a problem which has not been solved with such accuracy as to admit of any certain conclusion. But the argument derived from this has little weight; for it is not proved, nor even rendered probable by any analogy, or by any fact, that the augmentation of capacity is not proportional to the absorption of caloric: when this therefore is not proved, and when the supposition is not necessary to account for the phenomena, why should it be made? An augmentation of capacity is proved to take place; it must give rise to an absorption of caloric; and it may be sufficient to account for the whole quantity absorbed. It is an inconclusive mode of reasoning to say, that perhaps the augmentation may not be proportional, and that therefore a portion of caloric may exist in the fluid or air in some other state. “Since the existence of a cause,” says Crawford, “sufficient to account for the appearances, has been established by experiment, it seems inconsistent with the simplicity of the operations of nature to suppose, that other causes, for the existence of which there is no experimental proof, concur in the production of the same effects; for nature does nothing in vain; *et frustra fit per plura quod fieri potest per pauciora.*”

Some objections have been offered to Dr Irvine’s theory of latent heat, which it may be necessary to notice. The one of greatest apparent force was urged by Dr Black himself,—that supposing the absorption of caloric, and the latent state of the quantity absorbed, to arise from an increase of capacity in the fluid or vapour, no cause is assigned for the change of form. “The alleged fact of disparity between the capacity of ice and water for heat,” says Dr Black, “may be supposed to account for the thermo-

metrical phenomena just now recited ; but the principal fact or phenomenon is not accounted for by it, I mean the change of the solid into the fluid. Solidity depends on cohesive attraction ; but on what cause does fluidity depend ? Will it be said to depend on the absence or cessation of cohesive attraction ? I cannot imagine how cohesive attraction can entirely cease, or be suspended, or, if this should happen, how it should easily be again restored ? Nay we have evident proof, from the round form of the drops of liquids, that it is not in them entirely suspended, but only weakened to such a great degree, that the solid hard body is become a liquid. Now this is such a violent change, that I cannot help thinking it must depend on some powerful cause. It may be said, perhaps, that no other cause is necessary but the increase of sensible heat above a certain degree, together with some singularity in the nature of cohesive attraction ; such as that this attraction, though very strong at certain small and imperceptible distances, becomes suddenly very weak, when we increase, beyond a certain limit, the distance of the particles of matter from one another, and this increase of distance is produced by sensible heat. If this were true, the increase and diminution of distance by the action of sensible heat ought always invariably to produce each its appropriate effect on the power of the cohesive attraction ; as water, when its degree of heat is above 32° , is always liquid, so when its sensible heat is below 32° , it should always be solid. But this we know is not always the fact. Water, in some circumstances, can be cooled to 7 or 8 degrees below 32° without being congealed ; and many other substances exhibit the same phenomenon, by retaining their fluidity in some circumstances, after their sensible heat is diminished considerably below their ordinary congealing point. And I now ask, what is the cause which hinders the cohesive attraction from producing its effect, and changing the liquid into a solid ? When I find by experience, that, upon

disturbing such over-cooled liquids, a quantity of heat is extricated from them, which did not appear immediately before, and that, while this heat is extricated, a proportional part of the liquid congeals ; I cannot help considering this latent heat which was in it, as having been the cause of its protracted fluidity *."

There no doubt appears a difficulty in the circumstance here pointed out. The temperature of a fluid at its formation, is no higher than that of the solid from which it has been formed. By what cause, then, is its fluidity determined ; or by what operation can it exist, both in the fluid and solid form at the same temperature ? What more probable, than that a part, if not the whole of the caloric which becomes latent, produces the change of form, while another portion may be absorbed, from the augmentation of capacity which is the consequence of that change ?

This difficulty, I believe, arises solely from the difficulty of forming a clear conception of the balance of antagonist powers, according to the predominance of which the body exists in the solid or fluid state. The fluidity is determined by the operation of sensible heat counteracting the attraction of cohesion in the solid, until at a certain point the attraction is so far weakened as to admit of the particles passing into a new arrangement. It is obvious, that there is some point in the thermometrical scale at which, from this operation, the cohesion will be so far weakened, that the particles will move easily with regard to each other, a state which constitutes fluidity ; and that at another point, this remaining cohesion will be overcome, and a repulsion established between these particles ; and in this progressive operation, the ultimate effect in either case may take place at a point in the scale of temperature indivisible, so that we shall be unable to discover a difference of temperature on the one hand, or on the

* Black's Lectures, vol. i, p. 142.

other. Let heat be communicated to a piece of ice at 20° , its temperature is raised to 25° ; its particles, by this rise, are so far separated from each other, and its cohesion overcome. If more heat be communicated, the expansion continues to proceed, and the force of cohesion to be weakened. Let 32° be the point at which these powers are balanced, and at which the body is on the verge of change, the smallest divisible portion of heat, a portion by far too minute to be detected by our most delicate instruments, may subvert the balance, and effect the change. Indeed, ice cannot exist at 32° without melting. At this, therefore, it is past the last point of temperature consistent with solidity, which must be a fractional part below 32° .

The violence of the change which Dr Black mentions is not inconsistent with this view. If the expansion is progressive until it reach a certain point, beyond which it shall be so far weakened as to admit either of a new arrangement of the particles, or of a repulsion being established between them, it is obvious, that in this progression the smallest addition of force when the extreme point is arrived at, will be sufficient to produce the effect.

With regard to the fact mentioned in Dr Black's argument, that water may be cooled 7° or 8° below 32° without returning to the solid state, and the query, "What is the cause which hinders the cohesive attraction from producing its effect, and changing the liquid into a solid?" this is a difficulty, properly speaking, with regard to the theory of fluidity, and not peculiarly connected with the absorption of heat which attends that process, and is equally applicable to the one explanation as it is to the other. It may be urged against Dr Black's doctrine, If fluidity depend on a combination of the body with caloric, which combination, in the example of ice, takes place at 32° , and not lower, why is that combination not subverted, when the temperature of the fluid is reduced below this point? And it is even more difficult to remove the objec-

tion on this doctrine than on the other. In ascribing these changes of form to the prevailing force of one or two opposing powers, cohesion and the expansive energy of caloric, this phenomenon is explained on the hypothesis of a polarity in the particles of the substances in which it is observed; in consequence of which, in becoming solid, they are disposed to unite by certain sides in preference to others; the mere reduction of temperature, therefore, does not necessarily place them in those positions in which they are most disposed to unite, but, by agitation or motion impressed on the particles, some are placed in these favourable positions, or, by the contact of a solid particle, a surface is afforded, whence the exertion of the attraction will commence. But on the hypothesis of fluidity depending on a peculiar combination of caloric, it will be found equally difficult to explain, why, when the liquid is reduced in temperature a little below the point at which it had assumed the liquid state, this combination should not be subverted; or how its subversion should be effected by the contact of a solid particle, or by agitation of the fluid.

In relation to this question, Professor Robison contended*, that fluidity is not to be regarded as arising merely from the separation of the particles of the solid to such distances, that the attraction of cohesion is greatly weakened, but that a peculiar arrangement is established among the particles,—an equality of action, so that in all positions they attract each other with the same force; while, in a solid, there is an inequality of action, or they attract each other more in one direction than in another, whence all positions are not indifferent, and a force is required to change their arrangement. But admitting this view of fluidity, it is obvious, that these kinds of action, these dispositions or arrangements, may depend on the distances at which the particles are placed with regard to each other

* Notes to Black's Lectures, vol. i, p. 518.

by the powers of cohesion and sensible caloric : the separation, to a certain distance, diminishing inequality of action, or allowing the polarity to be exerted in a peculiar manner ; and there is no reason to suppose that such an arrangement in fluids is the result of a peculiar combination of the particles with caloric.

The conversion of a fluid into vapour is to be explained in the same manner : sensible caloric producing expansion, and separating the particles from each other. The only difference is, that this proceeds until the cohesion is overcome, and the particles repel each other ; and there is a fact with regard to this change, -- that it is resisted by pressure, or that, after it has been effected, pressure reduces the vapour to the fluid state, sufficient to prove that this view is just. Pressure, it is evident, can have only a mechanical effect. By resisting the separation of the particles, it may counteract the operation of sensible heat, and prevent the transition to the aëriform state, or, if applied to a vapour, it may cause an approximation of the particles, and favour the exertion of the cohesive attraction ; but we perceive not how it can prevent caloric from entering into a chemical combination, or separate it where it has been combined. This fact is a conclusive one, in proving that the body changes its form first, and that then the caloric is absorbed or disengaged ; for the pressure may influence the change of form, by its effects on the distances at which the particles are placed, but cannot influence a chemical combination if it did exist.

Some have imagined, that the constitution of the gases termed permanent is a proof of the combination of caloric ; the attraction of caloric to the bases of these gases being supposed to be so strong, that their change of form cannot be effected. This argument, which has been often urged, is stated with several others not more conclusive, by Robison, in his fifth note to Dr Black's Lectures. This circumstance, however, is no proof of a more intimate

combination of caloric, or a stronger attraction between it and the solid matter. There can be little doubt, but that the difference between the vapours and gases depends merely on the solid matter of the latter assuming the ærial form at lower temperatures than the former do ; and that could the temperature be sufficiently reduced, the latter, like the former, would be condensed.

For the reasons now stated, it appears to me, that there can be little hesitation in rejecting the opinion, that the absorption of caloric, which accompanies liquefaction and vaporisation, arises from any intimate combination of it with the body which has changed its form : and if the opposite view of these phenomena be just, it is a mistake to make any distinction between what are termed latent and sensible heat. The fact must no doubt be expressed, that when a body passes from the solid to the fluid, or from the fluid to the æriform state, a quantity of caloric is absorbed by it, which has no effect in increasing its temperature ; and in this sense the term latent heat, or latent caloric, may be employed. But we are not to consider this as existing in the body in a different state from the other portion of caloric it contains ; nor is it only at the transition of form that a larger quantity is necessary to produce in it a given temperature. At every subsequent increase of temperature, the fluid requires more heat than the solid, and the vapour more than the fluid ; and therefore, were such a distinction just, it would require to be said, that at every successive elevation of temperature, a portion of the caloric received by the fluid passed into a latent state. This is an important observation, and decisive of the question. In the theory of Black, the peculiarity in the absorption of caloric is considered as confined to the actual changes of form. But this is not the case : the liquid, after it is formed, does not suffer the same rise in its temperature from the same quantity of heat communicated to it that the solid does, nor does the vapour suffer the same

change as the liquid. At the change of form the body has acquired a new relation to caloric, in consequence of which it henceforth requires more heat to elevate its temperature a certain number of degrees: an absorption of a large quantity of caloric to keep up its existing temperature must therefore take place at the moment of change; and with the admission of this fact, the theory of Irvine is established, while that of Black cannot be maintained.

It may be supposed, that the difference of capacity in bodies, in whatever state they exist, may proceed from a chemical combination of caloric. By saying that different bodies, or different forms of the same body, have different capacities for caloric, we express the general fact, that in equal quantities, and at equal temperatures, they contain unequal quantities of this power. But may this not be owing to a more intimate combination, analogous to chemical union, of part of the caloric,—of that part of it in each body, which amounts to the difference of the quantity it contains, compared with another? This opinion is at once refuted, by the consideration, that were it true, the quantity of free caloric, or caloric of temperature, must in all bodies be the same, this being the very principle assumed; and hence, in equal reductions of temperature, they ought to give out equal quantities, proportioned to their quantity of matter. It is only when the reduction is carried to the lowest point of the thermometrical scale, that the excess which the one contains above the other, if it were chemically combined, ought to be given out. They give out, however, unequal quantities; and to account for this, the supposition, that the portion of caloric which one contains above another is in a state of chemical combination, cannot be assigned. Nor, as I shall immediately have to state, is there any foundation for the opinion, that caloric exists in such a state.

Whether, therefore, the question be considered as relating to the cause, why different bodies contain, at the

same temperature, unequal quantities of caloric ; or to the cause, why different forms of the same body follow the same law ; in neither case can it be supposed that a chemical combination of that portion of caloric which one contains more than the other, is the cause of the difference ; and as the phenomena are in both these cases the same, they must be ascribed to the same cause. In conformity to Dr Irvine's theory, and in language unconnected with any hypothesis, the general fact may be expressed, that caloric, whatever may be its nature, is a power diffused over matter ; the cause of that state of bodies termed Temperature ; having a tendency to diffuse itself until a common temperature is formed ; but, for the production of this temperature in *different bodies*, and in *different forms of the same body*, unequal quantities of this power are required.

SECT. VI.—*Of the Absolute Quantity of Caloric in Bodies.*

CALORIC, whatever may be its nature, must be contained in bodies in limited quantity. It may therefore be proposed as a problem, What the absolute quantity is ; or at what distance in the thermometrical scale, from a given temperature, would the point at which bodies would be without heat, be found ? The farther we reduce the temperature, the nearer we approach to this ; and could we arrive at it, it is evident that by commencing from it the thermometrical scale, the degrees on that scale would be a measure of the absolute quantity of caloric contained at a given temperature. We can never, however, expect, by any reduction of temperature, to abstract from bodies all the caloric they contain. But still it may be discovered by calculation from certain data, at what distance in the

thermometrical scale this point of absolute privation, or the real Zero, as it has been termed, would be placed. I have to state in this section the methods which have been employed, and their results.

The possibility of solving this problem seems first to have occurred to Dr Irvine, in consequence of his investigations on the capacities for heat. It is obvious, that if the quantity of caloric contained in bodies be proportional to their capacity, then from knowing that capacity in the different states in which a body exists, and the quantity of caloric which it absorbs or gives out when it passes from one state to another, we have the data from which the whole quantity existing in it may be discovered; that quantity bearing a certain relation, which the difference of the capacity of the body in its two states discovers, to the quantity absorbed or given out in the change of form. Thus, suppose the capacity of water to be to that of ice as 10 to 9, as has been estimated, water, at the same temperature with ice, that is at 32° , will in the same weight contain one-tenth more caloric. When water, therefore, is converted into ice, it must give out this tenth part, and by ascertaining what the amount of this is, we discover what the quantity of caloric is which water contains, or what quantity, numbered by degrees of temperature, will be requisite to raise it from the real zero to 32° . Supposing the quantity, according to Dr Black's estimate, to be 140° , this, according to the preceding statement, is the tenth part of the caloric which water at 32° contains; of course, the whole quantity is equal to 1400 degrees; or 1260 degrees, such as those contained in the water, now remain in the ice. But the capacity of this ice being one-tenth less than that of water, the quantity of caloric which would raise the temperature of water 1260° will raise that of ice 1400° . Hence either water or ice at 32° contains a quantity of caloric capable of raising its own temperature 1400

degrees, and of course the zero is at that distance, measuring, by the divisions of Fahrenheit's scale, from 32° *.

On these principles is founded the theorem which Dr Irvine gave for calculating the real zero. Without employing algebraical terms, it may be thus stated: The capacities of the solid and liquid being as the whole quantities of heat they contain, the difference between the numbers which express their capacities is to the number which expresses the capacity of the liquid, as the difference between the quantities of heat which each contains, measured according to the capacity of the liquid, is to the number of degrees which will express the quantity of caloric it contains from zero. The following general formula, therefore, may be given for the calculation. Multiply the number which expresses the quantity of heat absorbed when the body passes from the solid to the liquid, or given out when it passes from the liquid to the solid state, by the number denoting the capacity of the liquid. Divide the product by the number which expresses the difference in the capacities of the body in its two forms; the quotient will be the number of degrees of temperature between the freezing point of the liquid and zero, measured according to the capacity of the liquid. Or, if we take as the multiplier, the number which expresses the capacity of the solid, the quotient of the division will give the quantity of caloric contained in the solid at its melting point, measured by degrees according to the capacity of the liquid.

* Dr Irvine placed the zero at about 900° below 0 of Fahrenheit, from finding, as the result of his experiments, a different proportion between the capacities of water and ice. Instead of being as 10 to 9, as has been generally stated, he found it to be nearly as 10 to 8; and as Dr Irvine appears to have made the experiment to ascertain these comparative capacities with more care than any other person, his estimate would be to be preferred, if the discordant results on this question did not render all the numbers that have been given doubtful.

And, to bring these to degrees, measured by the capacity of the solid itself, it is only necessary to add the number of degrees absorbed in its transition to the fluid form.

All bodies having a common temperature, must be at the same distance from the commencement of the thermometrical scale. They will contain, indeed, different quantities of caloric; but this arises from the difference in their capacities, or from their requiring different quantities to produce the same augmentations of temperature. The degrees of temperature are the same, though the quantities requisite to produce these be different. If, therefore, water at 32° be distant from the zero 1400 degrees, all other bodies must be distant from it the same number of degrees; the number in each being measured by degrees according to its own capacity*. Hence, if this point be truly determined, it must turn out the same when determined by other methods on other bodies. And this agreement, if

* If this circumstance, the reckoning the degrees according to the capacity of the body referred to, be not attended to, the results cannot correspond; and there is reason to believe, that this has sometimes been overlooked. Thus, some authors, from the calculation in the text, founded on the capacities of ice and water, have stated the zero at 1260° below 32° . The caloric contained in ice at 32° is no doubt according to the data on which that calculation is founded equal to 1260° , measured by the capacity of water; but these degrees ought to be measured by the capacity of the ice; and as this is one-tenth less than that of water, this will bring them equal to 1400° . In like manner, the quantity of caloric in water at 32° , according to the same data, will be equal to 1400° above zero; these degrees being measured by the capacity of water. And, in all cases, the distance at which any body, at a given temperature, is from zero, ought to be stated in degrees measured by its own capacity; and if this be done, the distance of that point from a given temperature will in all turn out the same, though the real quantities of caloric they may contain will be different. For the following general formula, for calculating the zero, applicable to the measurement by the capacity

obtained, will be a proof of the justness of the principles on which the problem is solved.

Dr Crawford endeavoured to determine it by a calculation founded on the capacities of the two elements which, by their combination, form water, the quantity of heat extricated during their combination, and the capacity of the product. It is evident, that supposing the specific heats of the elements of water to be the same as their absolute heats, by knowing the former, the quantity of caloric given out during their combination, and the specific heat of the substance they form, we may discover the absolute quantities they contained, or the number of degrees at which they are distant from the zero. Dr Crawford calculated this to be 1550° from 50° of Fahrenheit, or placed the zero at 1532° below the freezing point of water*.

Gadolin instituted a series of experiments on this subject, which appear to have been executed with much care†.

either of the fluid or of the solid, and more comprehensive than any I have met with, I am indebted to my friend Professor Jackson. "Let C & c represent the capacities of the fluid and the solid respectively; H & h their absolute quantities of heat, as measured by thermometrical degrees, according to the capacity of the fluid; H' & h' , the same as measured according to the capacity of the solid:

$$\text{Then } C : c = H : h$$

$$\& C - c : C = H - h : H = \frac{(H - h) C}{C - c}$$

$$\text{Also } C : c = H' : h'$$

$$\& C - c : c = H' - h' : h' = \frac{(H' - h') c}{C - c}$$

Or, as the difference of the numbers expressing the capacities of the fluid and the solid, is to that expressing the capacity of either; so is the difference of their absolute quantities of heat at the point of liquefaction, estimated according to the scale of that capacity, to the distance on the same scale between the point of liquefaction and the absolute zero."

* Treatise on Animal Heat, p. 267. † Ibid. p. 457.

He ascertained the capacity of sea-salt, and the capacity of the solutions it forms with given quantities of water, and observed the degrees of cold produced in dissolving the salt in the various proportions of water: the results he obtained coincided with the supposition that the zero is 1400 degrees below 0 of Fahrenheit, or 1432° below the freezing point of water. Other experiments on the cold produced in the mutual action of snow and salt, and on the heat excited by the combination of sulphuric acid with water, agreed with this as nearly as from the delicacy of the experiments could have been expected.

The experiments of Lavoisier and Laplace with the calorimeter, gave, on the other hand, results altogether inconsistent with these, and with each other. From the heat produced by the mixture of water and quicklime, compared with the capacities of the lime, the water, and the mixture of the lime and water, the quantity of caloric contained in the water at 32° , or, in the equation they employed, x , was found $=1537.8$ degrees, according to Reaumur's scale, or 3460° according to Fahrenheit's; hence the zero is that number of degrees below 32° . An experiment, on the heat evolved by a mixture of sulphuric acid and water, compared with the capacities of the substances before and after mixture, gave $x=3241.9^{\circ}$ R., or 7294° F. A third experiment, in which the acid and water were in other proportions, gave $x=1169.1^{\circ}$ R., or 2630° F. And from the mixture of nitric acid and quicklime, in the proportion of $9\frac{1}{2}$ to 1, the result, as Laplace states it, was $x=\frac{1889}{=0.01783}$, a value, as he remarks, "physically impossible, and consequently proving the falseness of the hypothesis calculated on, if the specific calorics employed in the calculation were rigorously exact *.

This conclusion, taking into account this condition, no doubt follows both from the result of the last experiment,

* Mémoires de l'Acad. des Sciences, 1780, p. 386.

and from the discordant results of the others. "But it ought to be observed," adds Laplace, "that a very trivial alteration, at most a fortieth, in the estimation of the specific heats of the substances employed, will be sufficient to establish a correspondence between all our results;" for the quantities given out in these combinations, bearing so inconsiderable a proportion to the absolute heat, a slight alteration in the estimation of the capacity will have a very important effect in the calculation from which the zero is deduced; "nor can we affirm," he continues, "that an error so trivial has not crept into our experiments, and therefore they are neither favourable, nor adverse to the theory; and all that can be concluded is, that if the theory on which this calculation is established be just, the absolute heat of bodies the temperature of which is that of melting ice, must be at least 600 degrees of Reaumur's scale, (1350° of Fahrenheit's); for to make it a number less than 600° , it is necessary to suppose, in our experiments, errors greater than those of which they appear to be susceptible." With this admission, and considering that in no case can we be assured that the capacity of a body is ascertained with accuracy, so as to preclude the error of a fortieth part, and that with regard to many substances, the results of different experiments are much more discordant than this, there can be no hesitation in affirming, that the experiments of Lavoisier and Laplace do not invalidate the theorem of Irvine.

In addition to these experiments, Seguin has given calculations of the zero from experiments by Lavoisier, on the heat rendered sensible during the burning of different combustibile bodies*. From the heat produced in the burning of phosphorus he placed it at 1894° below the freezing point of water,—from that in the burning of hydrogen at 1663° , and from that evolved in the combustion of char-

* Annales de Chimie, t. v.

coal at 2709°. Mr Dalton also has from his experiments, or from facts furnished by Lavoisier and Crawford, calculated the zero, and has placed it still more remote from natural temperature. The following table exhibits the results, the numbers denoting degrees below 32 of Fahrenheit*.

From a mixture of 5.77 sulphuric acid and 1 water,		6400°
_____ 1.6 _____ 1 _____		4150
_____ 1 _____ 2 _____		6000
_____ 3 lime _____ 1 _____		4260
_____ 7 nitric acid _____ 1 lime		11000
From the combustion of hydrogen,	- -	5400
_____ phosphorus,	- -	5400
_____ charcoal,	- -	6000
_____ oil, wax and tallow,	- -	6900
_____ ether,	- -	6000

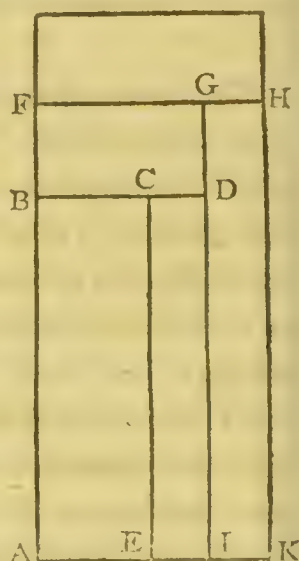
The same observations apply to these as to the preceding calculations. They are not less liable to errors, which, multiplied by the calculation, may give rise to such differences. These discordant results, therefore, only prove the difficulty to which the attempt to reduce the theorem to practice is liable, but do not invalidate the theory on which it has been attempted. If the capacities of bodies shall ever be determined with perfect accuracy, the question will assume a different form,—the place of the real zero will either be determined with certainty, or the falsity of the theory be demonstrated. At present we can expect neither. If we examine the table of capacities, we find such differences in the numbers affixed to the same substances by different experimenters, as sufficiently prove the difficulty of fixing them with such accuracy, as to admit of either conclusion. The investigation, too, is rather a

* System of Chemical Philosophy, p. 97.

subject of curiosity than of utility; and it is far from being what Professor Robison states it, that which “gives the chief importance to the whole doctrine of specific heats.” The importance of that doctrine consists in its giving the theory by which we account for the variations of temperature from chemical action; our knowledge of the relations between the specific heats of different substances enabling us to do so with accuracy, at that part of the scale of temperature at which they take place, though we know nothing of the absolute quantities of caloric they contain.

By a simple diagram, the principal facts relative to the capacities of bodies, the changes they suffer in changes of form, and the determination from these of the real zero, may be rendered obvious, and the preceding statements illustrated.

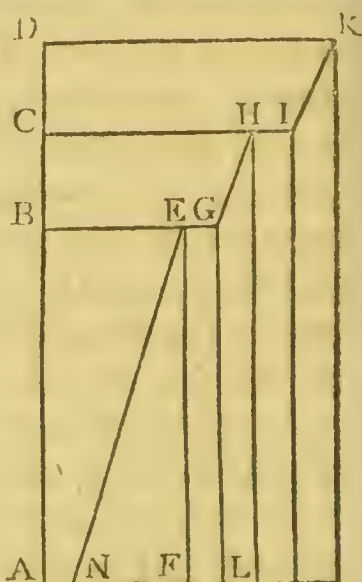
Let the line AB represent the scale of temperature, from the real zero A to any existing natural temperature B, and let the line BC denote the capacity of any body at that temperature, the rectangle CA will, on the theory, that the caloric contained in a body is proportional to its capacity and temperature, represent the whole quantity of caloric which that body at that temperature contains; and at any inferior temperature this will be represented by the rectangle formed by a line meeting at right angles the lines AB, EC. Let B be the point at which the body becomes fluid, its capacity is then enlarged, and this enlargement may be represented by prolonging the line BC to D. From this augmentation of capacity, a quantity of heat is absorbed, without producing any rise of temperature: this quantity, the latent heat of the fluid, is represented by the rectangle DE,



the sensible heat of the fluid by the rectangle CA, and the whole heat it contains by the rectangle DA. In raising its temperature, quantities of caloric must be communicated to it of course proportional to its capacity, and these might be represented by lines intersecting at right angles the lines BF, DG, this being continued until it be raised to the point at which it passes to the state of vapour. Suppose this to be at F, the augmentation of capacity which happens when this change takes place will be represented by prolonging the line FG to H, the quantity of caloric it absorbs from this augmentation by the rectangle HI. and the whole caloric which the vapour contains at the temperature at which it was formed, by the rectangle HA. To represent farther elevations of temperature, the lines AF, KH must be prolonged, and at any point the quantity of caloric contained in the vapour will be represented by the rectangle formed by these, the line AK, and a line intersecting at the part representing that point the prolonged lines AF, KH. By this simple diagram are thus represented, the relation of temperature and capacity, of latent and sensible caloric, the changes in the distribution of caloric accompanying changes of form, and the absolute quantity which any body at any temperature will contain.

This representation, for the sake of simplicity, has been given on the supposition, that the capacities of bodies are permanent, while it is probable that they are not so, but are progressive with regard to temperature, or become greater as the temperature rises. At the transition of a body to the fluid and æriform states, the capacity is suddenly enlarged; but, besides this, there is reason to believe, that in all its forms the capacity is gradually enlarged as the temperature is raised. We know it to be so in the æriform state; and both from analogy, and from the consideration of the effect of expansion on capacity, it may be inferred, that it is likewise the case in the liquid and so-

lid states. On this assumption, the same facts will be represented by the following modification of the preceding diagram *. The line AD will represent the scale of temperature from the zero A to a certain temperature above that at which the body passes into vapour, C being the point at which it suffers this change, and B the point at which it becomes fluid; the progressive augmentation of capacity which the *solid* suffers in the rise of its temperature from the zero to its melting point will be represented by the line NE, (AN representing its capacity at zero,) and the quantity of caloric which it contains at that point, being still solid, by the rectangle BF. The increase of capacity which happens at its fusion will be represented by the line EG, and the whole capacity by the line BG; the quantity of heat absorbed, by the rectangle GF, and the whole quantity the fluid contains at the temperature at which it has become fluid, by the rectangle GA. The gradual augmentation of capacity in the *fluid*, as its temperature is raised, will be represented by the line GH; and the heat it contains at the temperature at which it passes into vapour, by the rectangle HA. The enlargement of capacity attending that change of form is represented by the line HI; the whole capacity by the line CI; the quantity of caloric absorbed, by the rectangle IL; and the quantity of caloric the va-



* In this diagram it is assumed, that the augmentations of capacity, as the temperature rises, are regular, except where the changes of form take place, while it is possible that they be irregular. Any irregularity of this kind might be represented, by adapting to it, were it known, the lines NE, GH, IK.

pour contains at the temperature at which it has assumed that form, by the rectangle IA. Lastly, the increase of capacity in the *vapour* as its temperature rises, is represented by the line IK; its capacity at any temperature above its vaporific point will be represented by a line drawn at right angles from the point denoting that temperature, in the line representing the scale of temperature, until it meets the line IK, prolonged if necessary; as, for example, by the line DK; and the quantity of caloric it contains at that temperature will be expressed by the rectangle thus formed, KA.

In endeavouring to determine the question as to the place of the zero, and, of course, the question with regard to combined caloric, it has often been supposed, that the assumption of the permanence of capacity at all temperatures, is essential in the calculation. By the experiment, it has been said, by which we discover the capacities of bodies, we perceive that a given quantity of caloric added to a body, or abstracted from it at a certain temperature, elevates or depresses its temperature a certain number of degrees. By repeating the experiment on another body, or on the same body in a different form, we likewise discover that the same quantity of caloric, measured with accuracy, and communicated to it, or abstracted from it, produces a certain change in its temperature, different from that which the other experienced. We thus discover the relation subsisting between them, in the change which, at these temperatures, they suffer from an equal communication or absorption of caloric. But how do we know, that the same relation will subsist between them at all points of the thermometrical scale? Either of them at a temperature, 4, or 500 degrees below the medium temperature of the earth, may experience elevations or depressions of temperature from the communication or abstraction of a quantity of caloric different from what it would suffer from the same quantity communicated, or ab-

abstracted at natural temperatures. If this happen, it may be supposed, that from experiments as to the effect on their temperatures from quantities of caloric communicated or abstracted at natural temperatures, we can draw no conclusion as to the relative quantities of absolute caloric which they contain; and if such differences happened to both, and if the rate of variation was not the same in each, which there is little probability it should, any such conclusion might be very remote from the truth.

This has often been considered as a just conclusion. "If the capacities," says Seguin, "are not permanent, while bodies do not change their state, the determination of the real zero will always be inaccurate *." Professor Robison fell into the same mistake. "Dr Irvine's ingenious method of discovering the temperature of absolute privation," he observes, "presupposes the constancy of specific heat; or, if not constant, it supposes that we know the whole law of variation. Now both of these assumptions are highly improbable. In none of the progressions of natural operations that we are acquainted with do we find this constancy. It is much more analogous to other phenomena; to suppose that, in the temperatures near to that of absolute privation, the quantities of heat necessary for producing equal elevation gradually diminish, and this, perhaps, without end, like the distance of the hyperbola from its asymptote. It is equally probable that the law of diminution may be different in different substances. This will cause the measures of specific heats to change their proportions continually; and therefore the specific capacities observed in temperatures, all of which are far removed from that of the entire absence of heat, give us no means of obtaining the proportions of the accumulated sum of all the heats which has been received into the substances. It follows from this, that even although it should be

* *Annales de Chimie*, t. v, p. 252.

granted to Dr Irvine, that the heat which emerges, in mixing vitriolic acid and water, or in the freezing of water, is the difference between the absolute heat of the mixture, or the ice, and the absolute heats of the substances before mixture, or of the water before freezing, still we cannot ascertain those absolute heats, or the temperature of no heat *."

This view of the subject, is, however, incorrect ; and in investigating these questions it is of no importance whatever whether the capacities are permanent or not, or whether we know the rate of their variations, if, as is most probable, they do vary ; for, be the variations what they may, excluding the hypothesis of combined caloric, a body at any temperature will always contain caloric, proportional to its capacity at that temperature. This will be apparent, when we consider, that if it change its capacity, it gives out or absorbs, according as the change is diminution or enlargement, a quantity of caloric proportional to the change. Thus, suppose the capacity to be ascertained at 32° of Fahrenheit, and that, in the reduction of temperature 100 degrees below this, it remains unchanged : in falling each degree, the same quantity of caloric will be given out. Suppose the capacity is now diminished one-tenth, then in falling lower, one-tenth less caloric will be given out each degree than in the preceding period. But then, when the diminution of capacity happened, a quantity of caloric will be extricated equal to this deficiency of one-tenth all the way down to the zero ; and hence, when that point is reached the body will have given out, on the whole, just the same quantity of caloric it would have given out, supposing its capacity had remained unaltered. The only difference is, that in that case it would have given it out equally, an equal portion being parted with at all degrees of the scale in an equal reduction of tempera-

* Notes to Black's Lectures, vol. i, p. 507.

ture, while, in the case we have supposed, it gives it out unequally, or, at the point where the change of capacity happens, it parts with a quantity at once proportional to that change, and from that downwards gives out portions in equal reductions of temperature, regular but smaller than it would have done if that change had not taken place.

This may easily be illustrated by a reference to the first of the preceding diagrams. The line AB representing the scale of temperature from the zero A to any existing temperature B, and the line BC the capacity of any body at that temperature, the rectangle CA represents the whole quantity of caloric which that body at that temperature contains. At this temperature, which may be assumed to be a low one, the capacity of the body is enlarged, which is represented by prolonging the line BC to D; and if the temperature be raised to the point F, in the thermometrical scale, the rectangle FD will represent the quantity of caloric which it has received between that and B, where its capacity was enlarged. But it is to be observed, that when the change of capacity has taken place at B, the body not only requires more caloric to raise its temperature from that point than it did before, but, at the moment of enlargement, it must have absorbed as much caloric as will keep up its temperature, according to its enlarged capacity, from the real zero to the point at which the change happened: and therefore the whole quantity of caloric it contains, at the temperature F, is represented, not as those would suppose who conceive the permanence of capacity to be a necessary assumption in estimating the absolute quantity, by the united rectangles, FD, and CA, but by the rectangle FI. Lastly, suppose that at the point F, its capacity suffers another enlargement, to be represented by the line FH, it will not only require more caloric to raise its temperature henceforward, but it will absorb, at the moment of change, as much caloric as is requisite to keep up its temperature according to that

capacity from zero ; and if AF be farther prolonged, and be connected by a straight line with the line KH, likewise prolonged, so as to form the rectangle which is the figure of the diagram, this rectangle will represent the quantity of caloric which the body contains at the higher part of the scale of temperature, represented by the prolonged line. Now, if from knowing the capacity at that part of the scale of temperature, (which may be supposed to be a natural one), we seek to determine at what distance from it the real zero will be found, it is of no consequence, that at the points F and B, the capacities become less, because at the moment of such an alteration a quantity of caloric will be given out, which, added to what remains, will be equal to what would have been contained, though the capacity had remained unchanged.

It is also obvious, that it is unimportant whether the changes of capacity be more numerous than those represented in the diagram ; for at each change the same thing will happen which has been described, or whether they be changes of enlargement or diminution, or, lastly, whether they happen by starts, as represented, or proceed gradually from the zero. The permanence of capacity is therefore not essential in the general proposition with regard to the distribution of caloric in bodies ; but at whatever temperature we found our calculation, *the body will contain a quantity of caloric proportional to its temperature, and its capacity*, proceeding always on the supposition, that no caloric exists in it chemically combined.

Connected with the preceding investigations, is the question, whether caloric exists in bodies in a state of combination more intimate than that in which it produces temperature. This has no connection with the opinion already considered, that the caloric absorbed in liquefaction and vaporisation, enters into intimate union with the body suffering these changes of form, but rests on the result sup-

posed to be established, that in different cases of chemical action, the quantity of caloric rendered sensible does not correspond to the changes of capacity that take place. It is hence inferred, that there must exist a quantity of caloric in some other state than what the capacity indicates, probably, therefore, chemically combined.

It is on the state of the fact with regard to this, that this hypothesis is to be determined. If there is reason to conclude from experiment, that the absolute quantity of caloric in a body is proportional to its capacity, it follows, that no portion is in a more intimate combination than another; but if it shall appear, that the absolute caloric, as calculated from experiments, is not as the capacity, the opposite conclusion may be drawn. This is determined in the following manner. If, by a series of experiments on the changes of capacity from different combinations or changes of form, the zero is found to be at the same point in the thermometrical scale, it may be concluded, that the absolute caloric is proportional to the capacity; but if by calculation from different experiments, the zero is placed at different parts of the scale, the opposite conclusion will be established; for the determination of the zero depending on the relation which the diminution or increase of capacity has to the augmentation or reduction of temperature, it follows, that if in some cases augmentations of temperature arise, partly from a diminution of capacity, and partly from a portion of caloric chemically combined being set free, while in other cases they arise solely from diminution of capacity, the zero, as calculated from these alterations of capacity and of temperature, will vary; or if, in all cases, the augmentation of temperature arise partly from the one cause, partly from the other, as there can be no reason for supposing that a constant relation will subsist between these, a variation in the point at which the zero is fixed must be observed. If it turn out uniform, it

follows, that caloric is contained in bodies only in proportion to the capacity.

The experiments by Irvine, Crawford and Gadolin, it has been already stated, were favourable to the conclusion, that the quantities of caloric in bodies are in proportion to their capacities, that therefore none exists in a state of chemical combination. Irvine and Crawford found, that evolutions of heat were always accompanied with diminutions of capacity in the bodies concerned, and absorptions of heat with enlargements of capacity, and that these were proportional to each other, or at least the deviations were not inconsistent with that law, or were not greater than might be accounted for from the inaccuracies to which such experiments are unavoidably liable *. And Gadolin, in experiments made with the express view of investigating this question, found a perfect coincidence between the results and the known capacities of the bodies, so as to "put beyond all doubt, that the colds produced are entirely owing to the changes of the comparative heats, and that no part of the heat has been chemically combined."

The experiments, however, of Lavoisier and La Place, afforded results so discordant, as led them to incline to the opinion, that, besides the caloric in bodies proportional to their capacities, a portion exists in combination, part of which is evolved during their chemical action.

The admission of such a conclusion rests entirely on the presumption, that, in the experiments in which these discrepancies were observed, the specific heats of the bodies operated on had been accurately known, this being presumed before it could be decided that these differed from the absolute quantities of caloric. But as La Place himself states, "The precision with which it is necessary to know the specific heats of bodies, renders it very difficult to verify the theory, at least by the combinations which we have

* Crawford on Heat, p. 269.

employed, owing to this, that the absolute heat of bodies being very considerable, relative to that which they give out in their combinations, a small error with regard to their specific heats will produce a very great error in the absolute quantity of heat." And his candid admission, that an error of not more than a fortieth in the estimation of the capacities would be sufficient to give rise to these discordant results, at once prevents the above conclusion from being drawn. That it is impossible to ascertain, by the methods hitherto employed, the capacities of bodies with such accuracy as to exclude errors not greater than this, will be admitted by every one who has given any attention to this subject. If we examine the table of capacities, we find differences in the estimation of the capacities of the same substance, not merely of a fortieth, but of a tenth, or even a fourth. The capacity of alcohol is stated by Crawford 602, by Irvine 930; of sulphuric acid by Crawford 429, by Lavoisier 335; of tin by Crawford 70, by Wilcke 60. Many similar examples might be given; and indeed there are not many instances in which the capacity of a body, determined by two experimenters, coincides so nearly as one-fortieth. It is evident, therefore, that these experiments afford no support to the doctrine of combined caloric. The same remark applies to similar conclusions more lately drawn by Berard and Delaroche; they are founded entirely on the supposed accuracy of their estimation of the capacities of the gases, which, as has been already stated, there is little reason to admit even to an extent much within that which would obviate the conclusion.

Lavoisier and La Place stated another experiment, the result of which, in their opinion, cannot, by the admission of any supposed error, be reconciled with the others. It is that of the solution of nitre in water. A degree of cold attends the solution; and therefore, according to the theory, the capacity of the solution of the nitre must be greater than the mean capacity of the salt and the water. They

give it, however, as less; the calculated capacity being 0.88889, while the real capacity is only 0.8167; hence a rise, instead of a fall of température, ought to have attended the solution. Dr Irvine *junior*, however, found the capacity of such a solution of nitre to be 914 instead of 816. This agrees, therefore, with the result of the experiment. Gadolin had before made the solutions of sea-salt in water, to which La Place likewise refers, the subject of experiment; and had found, that the changes of temperature attending the solution correspond exactly with the changes of capacity. So far there are no just grounds for the conclusion, that any portion of caloric exists in bodies different from that which produces temperature.

There are some other facts, however, more difficult perhaps to explain. Nitre, a salt composed of nitrous acid and potash, contains a very large quantity of oxygen as one of the elements of the acid, and this oxygen seems to exist in it with the greater part of the caloric it holds in the gaseous form. This appears by tracing the formation of the nitre as far as the process can be accurately observed. When its acid is formed by the combination of nitrous gas with oxygen gas, there is no great elevation of temperature; hence much of the large quantity of caloric which exists in the oxygen gas must be retained in the acid, and when the acid combines with potash to form the salt, there is no great evolution of heat, and therefore this large quantity of caloric, traced from the oxygen into the acid, must also exist in the salt. And that it actually does, seems to be proved by the fact, that in the deflagration of inflammable substances with nitre, a high degree of heat is produced. Yet nitre does not appear to have a large capacity for caloric: it diminishes, as Berthollet has remarked, the specific caloric of water. The specific caloric of oxygen is nearly five times as much, according to Crawford's estimate, as that of water: since so much of this, therefore, remains in the nitre, it follows, that could

the absolute caloric in a body be estimated from its specific caloric, the capacity of nitre should greatly exceed that of water, and of course the capacity of its solution in that fluid should also be greater than that of pure water, instead of being less.

Again, when ammonia and muriatic acid, each in the state of gas, are combined together, the quantity of caloric extricated is far from being considerable, though in this case two gaseous bodies, by their union, pass into a concrete state; a change of form that might be supposed accompanied with a considerable change of capacity.

On the other hand, in decomposing water by a metal aided by the agency of sulphuric acid, a large quantity of hydrogen gas is rapidly extricated. Hydrogen gas has, according to every estimate, by far the largest capacity for caloric of any known body. We might suppose, therefore, that when a quantity is thus rapidly extricated, it would absorb much caloric, and that the temperature of the mixture from which it is evolved would be reduced, which is not sensibly the case. The case of deflagration affords a similar objection. From such facts, it is inferred, that the quantity of caloric in bodies is not always proportional to their capacities; that it must therefore exist in some other state, most probably in more intimate chemical union.

There may be a difficulty in some of these cases, yet there are some considerations which lessen its force.

In all of them the difficulty urged is derived from the assumed capacities of bodies which exist in the aerial form; and when we find so many errors in the determination of the capacities of solids and liquids, which can easily be subjected to experiment, and in quantities so large as to reduce considerably the magnitude of these errors, it cannot be supposed that the capacities of aëriiform fluids, which can be operated on in no large quantities, and are, besides, liable to peculiar sources of error, can be determined with much accuracy. There is every reason to

believe, that they are very imperfectly determined. The capacity of oxygen gas may, in Crawford's estimate, be too high, and of course we are led into error in inferring the quantity which must remain in its compounds from the quantity liberated in their formation by its combination.

But farther, in estimating the quantity of caloric liberated in combinations of the gases, or absorbed in their evolution, there is a source of deception in the quantities of the bodies concerned. When two gases combine, we imagine, from the large capacities of gases, that a large quantity of caloric should be evolved. But the quantities of caloric they contain are estimated, not by their volumes, but by their weights; and though the volume of the gases combining may be large, the quantity of matter is really small, and is almost nothing compared with the weight of the vessel in which the experiment must be made. Hence the caloric evolved must be inconsiderable, and is quickly diffused through the contiguous matter. In the combination of oxygen and nitrous gases forming nitrous acid, no great degree of heat appears to be produced. But the quantity of caloric evolved must be considerable, when it is considered that the quantity of gravitating matter in the gases is small, and that the temperature of the vessel is raised along with that of the new compound, so as to become sensibly warm: this product too, (unless water be admitted, which of course will absorb much of the caloric evolved,) remains in the gaseous state, and in its transition into nitre by combination with potash, an additional portion of caloric will be disengaged. In the union of ammonia with muriatic acid, each in the state of gas, the vessel in which it takes place becomes sensibly, though still only moderately warm. Yet, as is justly observed by Dr Higgins, with regard to this very experiment, "if a few grains of the gases can thus heat a vessel of this weight, during the union of their bases, it can be proved, that the liberated caloric was in quantity sufficient to main-

tain a vaporous state of the salt thus formed, or to make it almost red hot *.” In the opposite case of an evolution of heat, we are deceived in the same way. In the evolution of hydrogen gas, it is supposed that there should be a considerable reduction of temperature, from the large quantity of caloric which the hydrogen gas requires; but the weight of the hydrogen evolved is inconsiderable, compared with that of the materials from which it is disengaged, and the caloric, the abstraction of which reduces their temperature one degree, may, from this cause, contribute to the elevation of this quantity of hydrogen a number of degrees.

It has been shewn, by actual experiment, that where a gas is evolved in consequence of the chemical action of substances on each other, less caloric is rendered sensible than where the same action happens without the disengagement of the gas. Thus, Lavoisier found, that in adding an acid to a pure alkaline solution, a considerable degree of heat is produced from the combination; while, in adding the same acid to the solution of the alkali combined with carbonic acid, there is a production of cold; the carbonic acid gas evolved absorbing a large quantity of caloric, which would otherwise have been rendered sensible †.

From these considerations, it must appear, that until we have more accurate methods of ascertaining the capacities of bodies, and the changes of temperature to which alterations in their form or mode of existence give rise, we can draw no strict conclusion from facts such as those that have been stated against the principle, that caloric is contained in bodies in proportion to their capacities; nor any argument in favour of the hypothesis, that it exists in bodies in a combined state. We never observe, as Dr Ir-

* Minutes of a Society for Philosophical Experiments, p. 30.

† Mémoires de l'Acad. des Sciences, 1777, p. 431.

vine *junior* justly remarked, that caloric enters a body without raising its temperature proportional to the quantity that is communicated, unless there be, at the same time, a change of capacity; which change we can ascertain by experiment. Yet why should caloric, if it is capable of entering into intimate combination with bodies, not do so at parts of the scale of temperature at which we can make our experiments, as well as at parts of that scale which are removed from us, and where no direct experiment can be made? This consideration is probably sufficient to prove, that the supposition, that such combinations take place at these low temperatures, derives support only from the difficulty and obscurity in which the subject is involved.

The theory of Irvine, which regards caloric as thus existing in bodies in one state, is eminently distinguished by its simplicity, compared with the other. It embraces merely one principle,—that caloric, whether it is a material agent or a force, is distributed in all bodies, at all temperatures, according to their respective capacities; and that every change of temperature not produced by the direct communication of heat, arises from a change in the capacities of the bodies, from the action of which the variation has been produced. Under this principle, established to a great extent by experiment, as an ultimate fact, all the phenomena of temperature are arranged. Should even difficulties exist with regard to these, the hypothesis of combined caloric can scarcely be inferred from them, and it is supported by no independent proof. The materiality even of this power is doubtful; its agency, so far as it can be traced, is that of producing repulsion; it counteracts the attraction of cohesion, and there is little probability in the assumption, that it shall be liable to chemical attraction, and enter with bodies into intimate combination, so as to lose its characteristic properties. The agency and relations of a power so peculiar, exclude indeed all analogies from ponderable substances, and its laws

must rest on direct evidence alone, or the extension of analogies which that evidence affords.

From the diversity of opinions which have prevailed among chemists respecting the states in which caloric exists in bodies, several forms of expression have been introduced, which may be explained in this place.

Free Caloric is caloric in that state in which it expands bodies, and, accumulated to a certain extent, produces the sensation of heat. It is synonymous with the *sensible heat* of Dr Black, and with the *caloric of temperature* of some other chemists.

Specific Caloric expresses the relative quantities of caloric contained in equal weights of different bodies at the same temperature, or the quantity of caloric peculiar to any body. Thus we say that the specific caloric of water is to that of mercury as 28 to 1. The term is synonymous with the *Comparative Heat* of Dr Crawford. Others have used the phrase *Relative Heat* in a similar sense. Wilcke employed this term *Relative Heat* to denote the specific caloric of a body when estimated, not by the weight, but by the volume.

The disposition or property by which bodies contain certain quantities of caloric at any temperature, is named their *Capacity for containing caloric*. The term is used in a comparative sense; as when the capacity of any body, that of mercury, for example, is said to be so much, compared with that of another, as of water. Hence the phrase can generally be substituted for that of specific caloric, the cause being placed for its effect. The specific caloric is the quantity contained in any body, the capacity the property by which that quantity is contained; they must therefore be proportional.

Latent caloric, or *Latent Heat*, is the expression used to denote that quantity of caloric absorbed when a body changes its form. The expression is perhaps unnecessary,

the quantity of caloric which the body contains in its new state being a portion of its specific caloric, but it may be retained to denote the fact.

Combined Caloric is that portion of caloric supposed to be contained in any body chemically combined. I have already observed, that it is very doubtful whether caloric exists in such a state.

The *Absolute Heat* of Dr Crawford denotes the whole quantity of caloric which any body contains. It is expressed in the modern chemical language, by saying the absolute quantity of caloric contained in bodies.

SECT. VII.—*Of the Nature of Caloric.*

THE nature of that power which we denominate Heat, has long been a subject of discussion, and the question is not determined; for although the greater number of modern chemists have inclined to the opinion that it is a peculiar substance of great subtilty, some have maintained the hypothesis, that the phenomena which it exhibits do not depend on a material agent, but arise from some state, probably a vibration of their particles, which bodies can assume. Bacon appears to have suggested this hypothesis; finding, from a copious induction of facts, that the causes which give rise to increased temperature, and its effects, are in general such as excite motion among the particles of bodies, and that causes producing such motion are generally followed by rise of temperature, he concluded, “that heat arises from violent motion in the internal parts of bodies.” In pointing out the nature of this motion, he adds, that it is an expansive one, tending to dilate the body in which it happens; its tendency is also to rise upwards; that though the smaller particles dilate them-

selves, this motion is restrained, so that it becomes constantly alternating, or *vibration* performed with rapidity among the minute particles ;—in his own words, “ *Calor est motus expansivus, cohibitus et nitens per partes minores **.” This notion with regard to the nature of caloric was adopted by Boyle and Newton. The other opinion, however, continued to be more generally embraced. It considers caloric as a subtle elastic fluid, with which all bodies are penetrated. Homberg, Lemery, Boerhaave, and the greater number of chemists supported it, and though confessedly hypothetical, it seemed so probable, and explained the phenomena so satisfactorily, that it came to be generally received.

Its justness has however been called in question, and I may review briefly the arguments by which these different opinions are supported.

In favour of the existence of caloric as matter, it may be stated, that such a supposition appears to accord with the phenomena of temperature, its changes, and the effects these produce upon bodies with respect to expansion and change of form. If a body is increased in volume, it is natural to imagine, that some other matter, some subtle fluid, has been introduced into it, which has separated its particles, and the accumulation of this, by augmenting the expansion, may at length place them at such distances as to produce the fluid or aëriform state. Since temperature can be communicated from one body to another, it is natural to refer the distribution to the communication of this subtle matter. And if different bodies have their temperatures unequally raised by equal communications of this power, the phenomenon may be explained by the supposition of difference in density, or of affinity between the power itself and the matter to which it has been communicated. So far the effects produced by caloric and its re-

* Works of Lord Bacon, vol. iv. p. 328.

lations to matter in general seemed to be explained on the supposition that it is a peculiar fluid, the particles of which are mutually repellent.

There is only one phenomenon, the explanation of which is not so obvious, and which has been supposed to afford reason to doubt of the materiality of caloric. It is the production of heat by friction or percussion. Examples of this are familiar. If a rod of iron be beat upon an anvil, it becomes hot, and if the hammering be continued, its temperature rises to ignition. A rope rapidly revolved round a solid body will be so much heated, that it will catch fire; or the friction of two pieces of hard wood against each other will heat them so as to kindle them. The spark struck from a flint and steel is an example of the same kind.

In these cases it was supposed, that the caloric contained in the body is expelled by the repeated impulse arising from the friction or percussion forcing the particles nearer to each other. Some chemists, however, from the quantity disengaged, and the circumstances connected with its production, have endeavoured to shew that the explanation is insufficient, and have adopted the opinion of Bacon on the nature of caloric.

Rumford had observed, that in the boring of cannon, much heat is rendered sensible. To ascertain the quantity he fixed a solid cylinder of brass in a trough filled with water, and having adapted the borer to it connected with the machinery by which it is turned, it was made to revolve at the rate of 32 times in a minute. In an hour the temperature had risen from 60° to 107° , and in two hours and a half the water was brought to boil, the quantity being 18 lbs., and the apparatus itself, which was raised to the same temperature, weighing 15 lbs. The extrication of this caloric, he endeavoured to shew, could not arise from a diminution of capacity, since the capacity of the borings of the metal he found to be the same as that

of the solid metal. The circumstances of the experiment proved, that the air has no share in the production of the heat, since its access was prevented by the water surrounding the apparatus; neither does the water contribute to it by any chemical agency, since it undergoes no change; and, lastly, the caloric could not have been communicated by the surrounding bodies, since they were rather receiving it from the matter subjected to friction. He concluded, therefore, that any thing which any insulated body or system of bodies can furnish without limitation “cannot possibly be a material substance; and that it is extremely difficult, if not quite impossible, to form any distinct idea of any thing capable of being excited and communicated in the manner the heat was excited and communicated in these experiments, except it be motion *.”

Some experiments of a similar nature had previously been made by Pictet, which prove, in particular, that the caloric excited by friction is not produced by any agency of the surrounding air; since, by introducing machinery capable of producing friction into the exhausted receiver of the air-pump, and working it, heat was produced. This indeed had been established by Boyle, by causing two pieces of brass to rub against each other in an exhausted receiver, a sensible degree of heat being soon excited†. Pictet, in his experiments, found the heat to be increased by interposing some soft substance, as cotton, between the surfaces subjected to friction: the excitation appeared also to be connected with some electrical phenomena, whence he supposed electricity to be concerned in its production‡. Davy had reported some experiments, from which he drew similar conclusions. By exciting friction, he found heat produced, although the apparatus, as he conceived, was in-

* Essays, vol. ii, p. 493.

† Boyle's Works, vol. iii, p. 265.

‡ Essais sur la Physique, p. 197.

sulated by being placed on ice *in vacuo*; and by exciting it between two pieces of ice itself, he found so much evolved as to melt it. In this case the evolution of caloric could not be ascribed, it was supposed, to a diminution of capacity, since the water into which the ice was converted has even a greater capacity for caloric: nor could it arise from any chemical action of the atmospheric air, since ice is not acted on by this air, or by any of its principles: In other experiments, too, heat was produced when the friction was excited *in vacuo* *.

The question, with regard to the nature of caloric, probably does not admit, in the present state of our knowledge, of being satisfactorily solved. I can only offer a few observations on those facts and arguments which have a relation to it.

That the opinion which supposes it to be matter, affords a satisfactory explanation of the greater number of the phenomena arising from that power, can scarcely perhaps be denied. On the assumption of the existence of a subtle fluid, whose particles are mutually repellent, the expansion of bodies, their fusion, and vaporisation, may be conceived to arise from its introduction. It is also *a priori* sufficiently probable, that this fluid may have different relations to different bodies, and that from these differences it will produce upon them unequal effects: it may be propagated through them with different degrees of celerity, be contained in them in a given state in different quantities, and produce in them different degrees of expansion and of resistance to cohesive attraction.

The opposite opinion, that caloric is motion, considering it also as an hypothesis, does not afford an explanation of these phenomena equally satisfactory. The most general effect of heat is expansion; but if heat is mere motion or vibration of the particles of the heated body, how

* Beddoes's Medical Contributions.

is this effect produced ? Vibration is the alternate approximation and retrocession of the particles ; but from this state it is not evident, how permanent and uniform increase of volume can take place. Still less can this cause account for the great augmentation of volume which accompanies fluidity and especially vaporisation. The laws of the propagation of heat through bodies are likewise different from the established laws of motion. Were they the same, the propagation ought to be momentary through elastic bodies, and should be more or less rapid through others, according to their elasticity, which is far from being the case. Neither is any cause pointed out why it should be so slowly transmitted through liquids or airs. We are equally unable to account satisfactorily for its distribution in bodies, and the quantities of it required to produce given temperatures in different substances, or the portions of it absorbed when bodies change their forms, on any laws it could observe, supposing it to be any species of motion.

So far the one opinion is preferable to the other ; it remains only to inquire whether any proof can be given of the materiality of caloric.

The communication of temperature through a vacuum has been regarded as such a proof. This fact was ascertained by Pictet, who found, that a thermometer indicated increase and diminution of temperature, when suspended in an exhausted receiver ; and Rumford affirmed, that this happens when the thermometer is suspended even in the Torricellian vacuum. It is true, that even in the Torricellian vacuum, there is reason to believe a very subtle vapour is present, arising from the vaporisation of the mercury from the absence of pressure. But admitting this, the rarity of this vapour must be such, that it cannot, it has been supposed, be capable of transmitting vibrations so as to raise the temperature in a short time.

The radiation of caloric appears to be a proof still less equivocal of its materiality. A matter is thrown from heat-

ed bodies, which moves in right lines with velocity, is capable of reflection and condensation, raises the temperature of any body on which it falls, and which in every state preserves the properties of caloric. The existence of calorific rays in the rays of the sun, apart from visible light, though comprehended perhaps under the same fact, adds to the proof, that a peculiar matter exists, possessed of the properties of caloric, and distinct from every other.

The materiality of caloric appears so far to be established, or at least rendered probable, and there remains only the difficulty of explaining the phenomenon, from which the opposite hypothesis has been deduced,—the production of heat by friction. Several explanations have been proposed. Without discussing what is confessedly hypothetical, I may add the following.

By friction, percussion, or any other mechanical impulse, the particles of bodies must be thrown into vibration or a state of oscillation; they must alternately approach to and recede from each other. In their approach, part of the caloric interposed between their particles must be forced out, and in the corresponding retrocession, caloric must be absorbed. Of these propositions there can be no doubt, since it is proved by experiment, that any compressible elastic body, a gas for example, subjected to pressure, gives out part of its caloric; and that, on the contrary, in its expansion from the removal of pressure, it abstracts caloric from the surrounding bodies. The point then to be determined is, Whence is the caloric derived, which is absorbed by the body in a state of vibration, and which alternates with the quantity given out? If it were merely the quantity given out in the approximation of the particles, no permanent rise of temperature could take place. But if any other source can be pointed out whence it can be derived, the difficulty will be removed.

It is not improbable, I conceive, that the part of the body under friction, and giving out caloric in consequence of it,

may receive caloric from the portion at rest, owing to the elasticity of that agent, or its tendency to exist in a state of equilibrium. In the retrocession of the particles, the layer of matter in the state of vibration may rather admit caloric from the contiguous layer, and ultimately from the rest of the mass, than re-absorb that which had been evolved in the preceding approximation. In this way a current of caloric may flow towards the vibrating surface, and a constant evolution of it be kept up. The possibility of this will be confirmed, if an analogous case can be adduced in which this law is observed; and this seems to exist in the excitation of electricity by friction. By the vibration excited by the friction in the electric body, the peculiar matter which gives rise to the phenomena of electricity is conceived to be forced out, doubtless, by the particles being approximated by the vibration. Now the phenomena of electricity shew, that it is not re-absorbed in the corresponding retrocession of the particles, but that it forms an atmosphere round the electric body, or is carried off by others, while a new portion is received from the matter, in contact with the electric substance, and ultimately from the earth. Thus a perpetual evolution of electricity is kept up. Caloric may follow the same law, though from not having that relation which electricity has with regard to conducting and non-conducting matter, this is not so easily established; and if this be admitted, the production of heat from friction is explained.

Rumford supposed, that the body under friction could not receive caloric from the matter in contact with it, because it was constantly giving out caloric to that matter. But in this there is nothing contradictory; the vibrating body might give out caloric, which would be diffused in part over the surrounding matter, and might still receive from it caloric. It might also be supposed, that the temperature of the matter giving caloric to the body subjected to friction must be reduced; but neither does this follow,

as the progression may extend through the whole substance, and through the matter in contact with it, and the supply be sufficiently rapid to prevent any reduction of temperature, independent even of the quantity which it again received from the body itself, and by which its temperature will be raised.

The evolution of caloric from this cause is no doubt connected with diminution of capacity. But this is merely momentary, though constantly renewed. The experiment, therefore, of Rumford, by which he endeavoured to shew that the evolution of caloric from friction cannot be ascribed to diminution of capacity, is not adverse to this opinion, and indeed in any point of view is of no weight; for the capacity of the matter evolving the caloric was not ascertained while it was in the state of vibration, but after this had ceased, when of course it had returned to its usual state, and when this had even been accelerated and rendered more certain, by the metallic filings which were subjected to trial having been heated in the progress of the experiment by which their capacity was ascertained.

It is lastly to be remarked, that the difficulty may not be so great as at first it appears, nor the quantity of caloric produced by the friction so considerable, compared with the condensation which the friction must occasion. Berthollet, who has given an explanation somewhat similar to that which I have delivered, has justly observed, that a large quantity of caloric is requisite to produce even a small augmentation of volume in a mass of solid metal, and that of course a small reduction of volume, and therefore an approximation of the particles during friction far from considerable, may evolve a large quantity of heat *. In some more recent experiments, he has shewn, that the production of heat by percussion is owing to the reduction of volume in the body submitted to it. He subjected pieces

* Chemical Statics, vol. i, p. 412.

of different metals, gold, silver, copper and iron, of the same size, to the stroke of the press by which the impression is made on coin, and ascertained the heat produced by immediately throwing the piece of metal into water, having previously ascertained by experiment the relation existing between a certain temperature produced in the water, and the temperature of the metal plunged into it, so as to draw the conclusion to what temperature the metal subjected to the percussion had been raised. He established in this way the important fact, that the production of heat by percussion is limited: at the first stroke, the greatest degree of heat was produced, at the second, less heat was evolved, and at the third, still less, as will appear from the following numbers, expressing the degrees of heat of the centigrade scale produced in two pieces of copper submitted to this operation.

First stroke,	First piece, 9.69	Second piece, 11.56
Second stroke,	First piece, 4.06	Second piece, 2.5
Third stroke,	First piece, 1.06	Second piece, 0.81

Here, though the quantities differed a little from the difficulty of rendering the stroke of the engine uniform, there is in both a progressive diminution in the heat produced, and from both, on the whole, the same quantity of heat nearly is evolved, being from the one 14.81, from the other 14.87. The other metals gave similar results, affording only different degrees of heat. Thus, from two pieces of silver, the elevations of temperature, expressed in degrees of the centigrade scale, were as follow :

First stroke,	First piece, 3.44	Second piece, 4.56
Second stroke,	First piece, 3.25	Second piece, 1.19
Third stroke,	First piece, 1.50	Second piece, 1.12

After the third stroke, the temperature was either not raised, or was raised in a much lower degree.

Berthollet farther found, that the production of heat is accompanied with condensation in the metal: the specific gravity of the copper, before it was struck, was 8.8529, after the first stroke it was 8.8898, and after the second, 8.9081: that of the silver, previous to being struck, was 10.4667, after being struck it was 10.4838. The different metals too gave more heat as they suffered a greater condensation, copper having its temperature more raised than silver or gold, and its density being more increased by the operation. The conclusion is obvious from these facts, that the heat produced by percussion is owing to the condensation produced. It was also ascertained in these experiments, that the communication of temperature from one body to another by percussion is much more rapid than it is by mere contact, a fact which farther contributes to render probable the preceding explanation of the mode of evolution of caloric by friction *.

It has been endeavoured to determine the question with regard to the materiality of caloric, by ascertaining whether it is subject to gravitation, or has weight. It is difficult to make the experiment with accuracy, so as to exclude the operation of circumstances which influence the result, and hence some of the earlier experiments on this subject, those of Buffon, for example, in which a body appeared to increase in weight by being raised to a white heat, are entitled to no consideration; and those of Roebuck and Whitehurst † seem scarcely to have been made with sufficient care. Mr Whitehurst pointed out a principal source of fallacy in the ascending current of air from the scale in which the hot body is placed, and the consequent tendency of the portion of air beneath the scale, to restore the equili-

* Mémoires d'Arcueil, tom. ii, p. 441.

† Philosophical Transactions, vol. lxvi.

brium of pressure; and to this he justly ascribed the apparent diminution of weight which in his experiments attended the raising a body to a red heat. The contiguity, too, of the hot body to the arm of the balance, must in some degree heat it, and, by the expansion it causes, alter the equilibrium.

Dr Fordyce made the experiment in a more unexceptionable manner, by attempting to weigh not sensible, but latent heat, by finding whether the congelation of water, which is attended with an evolution of such heat, be attended with any alteration in the absolute gravity. A glass globe was selected, of nearly three inches diameter, and about 1700 grains of water being put into it, it was hermetically sealed; it weighed exactly $2150\frac{1}{2}$ gr., its temperature being brought to 32° , by having been put into a freezing mixture. It was again immersed in this mixture for 20 minutes, by which part of the water was frozen; and on being carefully dried, and put into the scale, it was found to have gained about the $\frac{1}{80}$ th part of a grain. This was repeated five times; at each time more of the water was frozen, and more weight gained. When the whole was frozen, it was found to have gained $\frac{3}{8}$ ths of a grain. But the temperature of the globe and contained ice, by having been kept in the freezing mixture, had been reduced to 12° of Fahrenheit. On allowing it to rise to 32° , it was found to weigh $\frac{1}{8}$ gr. more than when the water was fluid. The beam he employed was so adjusted, that with a weight of between 4 and 5 ounces in each scale, $\frac{1}{1800}$ th part of a grain made a difference of one division on its index. The air of the room was 37° of Fahrenheit*.

By this experiment, it appears that water, by freezing, an operation in which it evolves caloric, becomes heavier, and that of course the addition of caloric to a body renders it lighter; which, if admitted, appears to prove that

* Philosophical Transactions, vol. lxxv, p. 361.

caloric counteracts the attraction of gravitation, as it does that of contiguous attraction or affinity. The experiment was repeated by Morveau and Chaussier, and with the same result, the water being heavier after it had been frozen in glass vessels hermetically sealed, than it was before. Fontana, however, did not find that there was any difference in the weight of ice and water, the balance remaining in perfect equilibrium*.

Lavoisier introduced into a strong glass flask a small capsule, on which were placed six grains of phosphorus. Having closed it accurately, he weighed it, and removing it, kindled the phosphorus, by exposing it to the solar rays, concentrated by a small lens. When the vessel had become cold, it was again weighed, and not the smallest difference of weight could be discovered. In a second experiment, he put a pound of water into a thin glass flask, which he sealed hermetically, and then weighed with the most scrupulous exactness, in a balance, which, when loaded with from 18 to 20 ounces, vibrated with the tenth of a grain. The water was frozen, and the vessel, on being dried and again weighed, was found to be the same; no difference being discoverable whether it was weighed with the included matter in the state of water or of ice†.

Lastly, the experiment was made by Rumford. He took two Florence flasks perfectly alike, and putting into one a quantity of distilled water, amounting to 4107.86 grains, he put into the other the same weight of weak spirit of wine, sealing both hermetically, and suspended them from the arms of a very sensible balance, so as to be in exact equilibrium. They were exposed to an atmosphere of 29° of Fahrenheit for 48 hours. At the end of that time, the water in the flask was converted into ice, the arm of the balance to which it was attached preponderated, and the

* Journal de Physique, tom. xxvii. p. 268.

† Mémoires de l'Acad. des Sciences, 1783, p. 418.

increase of weight which it appeared to have gained by its freezing was found by what was necessary to restore the equilibrium, to amount to $\frac{1}{35904}$ of its whole weight at the beginning of the experiment.

The result appeared, therefore, to correspond with the experiment of Fordyce. Rumford, however, found reason to conclude that he had been deceived. In two bottles, as nearly alike as possible, he put equal weights of water and quicksilver, and suspending them to the arms of the balance, he allowed them to cool 30 degrees, but without either of them acquiring or losing weight; yet, from the respective capacities of water and quicksilver, the former must have given out much more caloric than the other. He performed again the first experiment with every possible precaution, exposing the equal bottles, with water and spirit, small thermometers being included, to a cold atmosphere for 48 hours. At the end of that time the two bottles were in the most perfect equilibrium. He repeated the experiment several times, and in no instance did the water on congeling appear either to gain or lose weight. But if the bottles were weighed when they were not precisely of the same temperature, they would frequently appear to have gained or lost, either from the vertical currents which they caused in the atmosphere on being heated or cooled in it, or from unequal quantities of moisture condensed from the atmosphere on their surface, or from these causes conjoined*.

From the whole of the experiments on this subject, it may be concluded, that if caloric be subject to gravity, its weight cannot be ascertained by experiment. It is obvious, that this does not afford any presumption against its existence as a material principle; and when its extreme subtilty, demonstrated by the facility with which it penetrates

* Philosophical Transactions, 1799, p. 179.

all bodies, is considered, we cannot expect any other result ; nor would these experiments have been worthy the attention bestowed on them, had it not been for the singular appearances which were at first obtained.

In reviewing the arguments in favour of the materiality of caloric, it will probably appear, that the only conclusive one is that derived from its radiation, and from the existence of calorific rays in the solar beam ; and with regard to these, there are still the difficulties of how far radiant caloric is an insulated principle distinct from the surrounding medium, how far the solar calorific rays are connected with light, and how far these rays and the heating rays discharged in bodies at an elevated temperature are the same. Those too who have denied the materiality of caloric have embarrassed themselves with the hypothesis of Bacon, that the heated state of bodies arises from vibration of their particles,—an hypothesis possessed of no advantage, and which affords no adequate explanation of the phenomena. But the subject need not be considered under this limited view. Caloric, if its materiality is not admitted, may be regarded as a general force, producing repulsion ; and were it not for the facts with regard to its radiation, this view would perhaps be that most conformable to our present knowledge of the phenomena. And when we consider the intimate connection of this power with light, the connection of both with electricity, and the obscurity which exists with regard to the nature of all these agents, we shall scarcely venture to adopt a decided opinion ; nor can we regard any theory which can at present be advanced as perfectly satisfactory.

SECT. VIII.—*Of the sources of Variations of Temperature, and the applications of these to Practical Chemistry.*

THE consideration of the subjects announced in the title of this section will conclude the Chemical History of Caloric.

As the tendency of this power is to diffuse itself over bodies until an equilibrium of temperature is established, this would be attained, were there no causes to counteract it, and the temperature of the globe would become stationary at the medium between the temperatures of the substances of which it is composed, or rather the temperature would have been always uniform, and proportional to the quantity of caloric assigned to the earth.

Such an uniformity is, however, obviated by the constant operation of various causes; and no where do we trace more perfect arrangement than in that by which a certain range is established, admitting a succession of changes adapted to those operations that require it; but restraining these within certain limits, so that extremes, either of heat or cold, are counteracted, and are prevented from spreading over the globe.

The great source of natural heat is the solar rays. These pass through the atmosphere without much effect, and it is only when arrested by opaque bodies that heat is excited. As every part of the earth's surface is not equally and at all times exposed to the action of the solar rays, inequality of temperature giving rise to variety of climate, and change of season must be produced. The extreme of temperature, however, which might prevail, and accumulate in those parts of the globe most exposed to this source of heat, is counteracted by certain general causes constant in their operation, which restrain it within certain limits.

The atmosphere, in particular, serves this important purpose. When the earth is much heated, the air incumbent on it receiving caloric is expanded, becomes specifically lighter, and ascends; its place is supplied by new portions of air from each side, which in their turn are heated, expanded, and rise. An ascending current is thus established, by which the accumulation of heat is prevented where it is already abundant, while the warmer air must, by the constant succession, be propelled to colder climates, and in its course gradually parts with the caloric it had received.

This is the simplest view of the agency of the atmosphere in equalizing temperature, and is that which is usually delivered. A more minute examination of the subject discovers a more refined adjustment in the relation of solar heat to the temperature of the earth.

When the air heated at the surface ascends in the atmosphere, it becomes subject to less pressure as it ascends, and its rarefaction is therefore further increased. That rarefaction is accompanied with an increase in its capacity for heat; hence its temperature falls progressively without caloric being abstracted from it. It thus continues to ascend, and to fall in temperature, until it reach a height, when its density and temperature are the same with the air around. Its ascent then ceases, and at the same time it can communicate no portion of its heat to the air beyond this; for the communication of heat depends on difference of temperature, which here does not exist. There can therefore be no conveyance of heat into the interplanetary space, by the medium of the atmosphere, and the air retains nearly the whole heat it had received at the surface. This ascent of heated air takes place principally from the hotter parts of the earth's surface, that is, towards the equator. To restore the equilibrium, the surrounding air must necessarily press in; a current is thus determined at the surface from the poles, which interrupted as

it may be by local causes, must still constantly operate: To supply this an opposite current must take place in the higher part of the atmosphere from the equator, descending to the poles. This air as it descends becomes subject to greater pressure, whence it is condensed; its condensation is accompanied with a proportional diminution of its capacity for heat, and it thus gives out the excess of caloric it had formerly received, and which from its enlarged capacity it had retained.

By this arrangement the extremes of temperature at the surface of the globe are moderated. There is a constant abstraction of heat from the equatorial regions where it would otherwise accumulate, and a constant transfer of it to the polar circles where it is deficient; and the greater the direct communication of heat is to the former, the more rapid is the transfer of it by the medium of the atmosphere to the latter. And this law operates with augmented energy, according to the difference of temperature, over the whole intervening space.

It seems to follow, in consequence of this, that the temperature must rise towards the poles. Heat is constantly communicated there without any equivalent abstraction: of this heat a portion must be conveyed to the interior, but this must always be with a decreasing temperature, that is, the first or exterior layer will be at a higher temperature than the second, the second than the third; the accumulation, therefore, will be at the surface to a certain extent, and a progressive augmentation take place.

Hence also the mean temperature of the earth must have risen, and must continue to rise. This may be inferred from the constant communication of solar heat, and from the consideration that this is only in part discharged. The atmosphere, it appears, conveys no caloric by direct communication beyond a certain height; and what it abstracts from the hotter, it communicates to the

colder parts of the earth's surface. The only portion of heat discharged is by radiation ; but this is dependent chiefly on an elevated temperature, and must take place therefore principally from those parts where such a temperature prevails. Of the heat communicated, however, to these parts, a portion only is discharged by radiation, another portion being constantly abstracted by the atmosphere, and conveyed to distant parts at a lower temperature, where radiation must be comparatively inconsiderable. Hence, of the heat communicated, part is retained, and of course the mean temperature of the earth must rise.

With this rise there is a tendency to equalization of temperature over the surface of the earth. There is a constant transfer of heat from the equator to the poles ; the temperature at the latter must rise slowly, since there is not equivalent abstraction ; the temperature at the former can suffer little augmentation, for if it did, the discharge of heat by radiation, and the abstraction of it by the atmosphere would be proportionally increased. In all the portions of the intermediate space between the poles and the equator, the same law will operate, though with decreasing force ; and thus, over the whole surface, there is a tendency to equality of temperature, which, as the result of general causes, constant in their operation, will finally be established.

Lastly, there are limits within which the progression must be restrained. The temperature may continue to rise until it is so far augmented at the surface that the quantity of caloric discharged by radiation will be equal to the quantity received by the solar rays ; and beyond this it cannot proceed. How far this stationary temperature may be from that which at present exists, may not be easily determined. But if the increase of heat be accompanied with its more equal diffusion, it may not, as I have re-

marked in the illustration of this view *, “ proceed much beyond that which now prevails at the hotter parts of the earth; for at this, when extended over the whole, the quantity of caloric radiated may be equal to that received ; and even if it were to rise higher than this, still, from gradual changes in the laws of organized matter, or in the species of living beings, not greater than what seem to have occurred in the past revolutions of the globe, the existing temperature might be sufficiently compatible with the continuance of animated existence, and with an order not very different from that which now prevails.” There is, therefore, no ground, on the one hand, for the speculation, which some have advanced, of indefinite refrigeration ; nor, on the other, for that of unlimited increase, in the temperature of the globe ; “ but the final result must be a state of permanence and uniformity, the continuance of which is secured, by the very circumstance, that if it is deviated from the deviation must check itself.”

The agency of water is likewise of considerable importance in relation to the temperature of the globe. It not only, by its mobility, diffuses and equalises heat by the medium of the ocean, but by its changes of form introduces other modifications. In passing into vapour from heat, it absorbs caloric without increasing in temperature : this vapour ascends in the atmosphere ; when the heat diminishes, or when waisted to colder regions, it is condensed, and gives out the caloric it had absorbed. In seasons or situations where the cold becomes still more intense, water is congealed ; and in suffering this change it evolves caloric, to moderate the progressive reduction of temperature. When warmth is restored, it returns to the liquid state, absorbs caloric, and retards the approaching heat. The transition of seasons is thus moderated ; sudden and

* Transactions of the Royal Society of Edinburgh, vol. vii, p. 430.

extreme variations are guarded against, and the temperature of the globe every where preserved more uniform.

The range of natural temperature is comparatively moderate. The mean temperature is probably every where the same at a depth sufficient to exclude completely the influence of the variations of atmospheric temperature; but even at a considerable depth it differs considerably in different countries, as is shown most easily in the temperature of springs. The solar rays being the great source of heat, the difference depends of course principally on latitude, though it is also influenced by elevation, and by distance from the sea. The average annual heat increases from the poles to the equator; in the torrid zone it is from 75° to 80° , in moderate climates 50° or 52° , and towards the polar regions 36° . The extremes over the whole globe at the surface extend from a few degrees above 100° of Fahrenheit to 50° below the zero or commencement of the same scale. In tropical climates the heat in the shade occasionally rises to 105° or even 110° . The latter temperature has been observed in Egypt. At Senegal the air in the shade is usually at 94° , and is frequently at 111° by day. At Pondicherry, it is said to have been at 113° or 115° *. With regard to cold, in northern climates—Siberia and Hudson's Bay, the temperature is every year so low as to freeze quicksilver. At Hudson's Bay, the spirit thermometer was observed in the open air to stand at -50° †, and there is no reason to believe that any natural cold yet observed much exceeds this. At one time, indeed, it was supposed, that much more intense colds prevailed, the mercurial thermometer having been observed to sink 300 or 400 degrees below the freezing point of water; in one case observed by Hutchins, even to 490° ‡.

* Kirwan on the Temperature of different latitudes, p. 93, &c.

† Philosophical Transactions, vol. lxxvi, p. 271.

‡ Ibid. vol. lxxiii, p. 386.

But this, as has been already remarked, is a deception arising from the freezing of the quicksilver in the thermometer, and the contraction which it experiences. Hence, when at the same time observations were made with a spirit thermometer, the descent was not greater than what corresponded to -46° . The cold of America even exceeds that which prevails under the same latitudes in Europe: we have, therefore, no reason to believe, that in the old world more intense natural colds occur than in the new, and from the descriptions given of their effects, they appear as severe in North America as in the north of Europe or Asia. The decrement of temperature, according to elevation in the atmosphere, is at the rate nearly of one degree of Fahrenheit's scale, for each 300 feet of ascent.

The range of temperature, as produced by artificial arrangement, is much greater. Our power of producing cold is not indeed great, compared with that of exciting heat. The cold we obtain by freezing mixtures does not much exceed 100 degrees below the freezing point of water. Fourcroy and Vauquelin, by a mixture of snow and muriate of lime, previously cooled, effected a reduction of temperature to -65° of Fahrenheit, when the temperature of the atmosphere was not much below freezing. Mr Macnab, from a mixture of snow with diluted sulphuric acid, obtained a cold equal to $-78\frac{1}{2}^{\circ}$ of Fahrenheit. And Mr Walker, by successive cooling of the materials, obtained from diluted sulphuric acid and snow, a reduction to -91° , or 123° below the freezing point of water. The highest heat that has been measured is equal to about 160° of Wedgwood's, or $21,877^{\circ}$ of Fahrenheit's scale. This was the temperature of a small air-furnace belonging to Mr Wedgwood, and is superior to that which is necessary to fuse cast iron, or to bake porcelain. The heat in the focus of a powerful lens or speculum from the concentration of the solar rays, is still more intense, as is also that

excited by a stream of oxygen gas directed on burning charcoal; but of these we have no exact measurement.

Were the chemist restricted to those variations of temperature which occur in nature, he would be little more than an observer of her operations, since these are too trivial to have much influence on the operations of art. It is in our power, however, to produce more intense degrees, both of heat and cold; and in the remaining part of this section I have to state the means by which these are obtained, and the various contrivances by which they are applied and regulated. This will include a description of several of the most important operations and instruments of Practical Chemistry.

THE sources of heat which are under the control of art, and which, by peculiar arrangements, may be increased and applied, are the Solar Rays, Electricity and Galvanism, Condensation, Mechanical action between solids, including Friction and Percussion, and Chemical action, to which head Combustion belongs.

The Solar Rays are powerful in producing heat. In the open air, a thermometer is raised, by free exposure to them, to above 100° ; and when inclosed, so as to prevent the effect of a current of air, it may be raised much higher: in some experiments by Saussure, it was raised to 201° ; the temperature of the external atmosphere being 75° : and Professor Robison, in repeating these with a similar arrangement, raised the thermometer to 237° of Fahrenheit's scale*.

By concentration of the rays by a lens, or by a concave mirror, heat is excited to a degree of intensity nearly c-

* Black's Lectures, vol. i, p. 546.

qual to what can be produced by any other arrangement. In the focus of very large burning glasses, the heat excited is sufficient to melt the greater number of the metals and the earths, and to dissipate many other substances in vapour. It appears from the experiments of Macquer, that a greater heat may be excited by a concave mirror than by a lens; but the former is inconvenient, and indeed scarcely practicable in its application, from the rays being reflected upwards. The use of either, indeed, is very limited; for the heat, though powerful, is excited only on a small point; hence it can be applied to scarcely any other purpose, than to discover the changes which bodies suffer from intense heat. Rumford has shewn, that the intense heat obtained in the focus of a lens arises entirely from the concentration of the rays of light, and not, as some had supposed, from their power being augmented by a change in the direction of their motion; the same quantity of solar light, directed on the blackened surface of a metallic vessel containing water, producing in it the same total rise of temperature, whether the rays were parallel, or were made to converge by a lens.

The Electric Discharge is capable of producing a very sudden and great heat. If from a powerful battery, and transmitted through metallic wires of small diameter, even those metals which are least fusible are instantly melted. The electric spark, as I shall afterwards have to remark, affords a convenient mode of applying heat to effect the combination of gases.

The Galvanic Discharge is likewise powerful in exciting heat. On establishing a communication between the extremities of a galvanic battery, a high temperature is excited at the point where the communication is momentarily completed and interrupted; and in this way every combustible body may be made to burn, and by a powerful galvanic arrangement, almost every substance may be fused or dissipated in vapour. Or if a fine metallic wire

form part of the circuit, it is melted by the heat which the galvanic energy excites in its passage.

The production of heat from Condensation is best exemplified in substances which are highly compressible and elastic, consequently in aëriform fluids. It has been long known, that by condensing a gas by mechanical pressure, its temperature is raised; that in allowing it to expand again, its temperature falls; and that by rarefying it farther, a degree of cold is produced. I have already alluded to these facts, as illustrative of the theory of the capacities of bodies for caloric. I have now to state them rather more in detail.

The changes of temperature, from rarefaction and condensation of aëriform fluids, as they are indicated by a thermometer suspended in the air, amount only to a few degrees of Fahrenheit. The rise and fall of the thermometer, however, are very sudden, and this led Mr Dalton to suspect, that the real change is greater than it appears to be from the indication by the thermometer; but that the inequality exists only for a few seconds of time, owing to the containing vessel having a surface so much more extensive than the thermometer, that it speedily checks the change of temperature, by abstracting, or by yielding caloric. The quantity of matter, too, in the bulb of the thermometer, being so much greater than that in the rarefied air, is unfavourable to its affording an indication of the real change. Thus the phenomena agree with the supposition of great heat or cold being produced by the condensation or rarefaction, but existing only for a very short time*. This is also proved by the fact observed by Lambert, that, in rarefying air, the cold is greater the more quickly the rarefaction is performed.

This view accords, too, with a fact more recently established, that, by a sudden and great condensation, a high

* Manchester Memoirs, vol. v, p. 515.

temperature, equal even to ignition, may be produced. A luminous appearance had sometimes been observed from the discharge of an air-gun in the dark *. The experiment was repeated before the French National Institute. From the air rapidly compressed in the ball of an air-gun, so much heat was disengaged from the first stroke of the piston, as to set fire to a piece of fungus match placed within the pump. And if the body of the pump be terminated by a moveable end, formed of a piece of steel with a glass lens in its centre, at the stroke of the piston a ray of vivid light is seen in the inside †. An instrument has since been introduced, constructed on this principle, by which tinder is kindled. It is merely a condensing syringe of brass, with a steel rod about 10 inches long, and 5-8ths of an inch in the bore, with a cavity at the bottom containing the tinder. On pushing down the rod very suddenly the tinder is kindled, and by the turn of a skrew can be exposed to the air.

The theory of the effect of this instrument (the Condensing Syringe) is not very well ascertained. It has been ascribed to the rapid condensation of the air, evolving so much heat as to kindle the tinder. But there is a difficulty with regard to this; for the condensation being progressive, and the piston and the sides of the tube being composed of matter which is so perfect a conductor of heat, the heat ought to be abstracted as it is evolved, and there is no very obvious cause how it can be accumulated at the end of the tube: and according to the experiments of Desmortiers ‡, it is only when atmospheric air or oxygen gas is condensed in the tube that the tinder is kindled; the other gases do not produce the effect. This would lead to the suspicion that the effect depends on the

* Nicholson's Journal, vol. iv, p. 280.

† Ibid. vol. ix, p. 302.

‡ Ibid. vol. xxxiii, p. 227.

condensation favouring the combination of the oxygen with the inflammable matter, aided by the degree of heat that is excited; and under this point of view, the result would fall to be considered as a particular case of the general result established by Grotthus, that combustion is much dependent on the degree of rarity or condensation of the aërial matter. There is one fallacy indeed to which these experiments are liable, that with the other gases, should even the tinder be ignited, it will be instantly extinguished from oxygen not being present to support its inflammation. But this is obviated by using tinder impregnated with nitre, with which the result is found to be the same. There is another objection, to which this theory of the instrument is liable, that liquid substances, as alcohol, or soft substances, as phosphorus, are not kindled; which they ought to be, especially the last, if the effect depended on the combination with oxygen from its condensation. This renders it probable, that part at least of the effect depends on the intense mechanical motion and vibration produced in the solid body by communication from the rapid motion of the air.

Biot made the experiment of causing the union of oxygen and hydrogen gases, by compressing rapidly a mixture of them in the syringe of the air-gun. It is a hazardous one, as, in two out of three times that it was repeated, the barrel was burst by the explosion *. It is doubtful whether the compression in this case first causes the combination of the gases by the approximation of their particles, and then the evolution of heat as the consequence of this, or whether it merely produces such a heat as causes the combination: it is probable, however, from the preceding experiment, that the latter is the case.

That species of mechanical action which excites strong

* Nicholson's Journal, vol. xi, p. 303.

vibration in the particles of solid bodies, as Friction and Percussion, is productive of increased temperature. Of heat from friction we have many familiar examples. Two pieces of hard wood rubbed against each other are so much heated as to be kindled; and among savage nations, this method is had recourse to, to procure fire. The friction on the axle of a loaded carriage is sometimes such as to cause it to take fire, as is that from a rope made to revolve rapidly round a solid body. The intensity of the heat from friction depends not only on the force of the friction, but also on the state of the bodies subjected to it, with regard to hardness, elasticity, and other qualities. Scarcely any accurate experiments have been made on this subject. It is known, however, that the hardest substances do not afford the greatest heat. A table is given in Nicholson's Journal, (vol. viii, p. 218), of a series of experiments on the heat produced by rubbing different woods against each other; whence it appears, that the heat produced is not either directly or inversely as the hardness.

The heat from percussion is no doubt produced in the same manner as that from friction; and is easily carried to the same extent. By hammering an iron rod on the anvil, it is raised to a red heat; and the sparks struck from steel by a flint consist of particles of steel heated by the percussion, and rising to a state of ignition by suffering combustion in passing through the atmosphere. Hence, in making the experiment *in vacuo*, the particles struck off are not luminous, though their temperature is probably not far distant from a red heat. Such a temperature can be produced from mechanical action alone, as we find it to happen in incombustible matter. Putting aside the examples from phosphorescent bodies, which are fallacious, this is proved by a decisive experiment made by Mr T. Wedgwood, that of bringing a piece of window-glass in contact with a revolving wheel of grit;

it became red hot at its point of friction, and gave off luminous particles, which were capable of inflaming gun-powder *.

I have already stated the difficulty with regard to the explanation of the increase of temperature from these causes, and its relation to the theory of caloric. It can scarcely be doubted, that it is chiefly to be ascribed to a momentary diminution of capacity, from the approximation of the particles of the body under friction or percussion. It is possible, that the excitation of electricity, which will accompany the friction, may have some share in its production.

Chemical action is an abundant source of variation of temperature; the temperature being sometimes elevated, sometimes reduced. The theory of both changes has already been explained: More immediately they may be ascribed, according to the view which Berthollet has taken of the subject, and which has been stated under the Chapter on Affinity, to the condensation arising from chemical action, modified by the change of form which so frequently accompanies it. Or, ultimately, they depend, according to the theory of Irvine, on the change of capacity which follows combination, heat being produced when the capacity of the product of the combination is inferior to the mean of the capacities of the substances combined, and cold where it is superior to that mean.

Of the varieties of chemical action productive of heat, and indeed of all the sources of increased temperature, Combustion is the most important, both for common purposes, and in the operations of chemistry. To explain in a general manner the principles on which combustion is excited and applied, it is necessary to observe, that it is dependent on one of the constituent principles of the atmosphere,—oxygen gas. At temperatures which usually

require to be considerably elevated, this principle combines with combustible or inflammable bodies, the combination is attended with the production of heat, and in general with the evolution of light ; and it is this which constitutes combustion or burning.

We thus perceive how much combustion must be dependent on a due supply of atmospheric air to the combustible body ; and accordingly it is more rapid the more freely the air is applied. On this is founded the construction of Furnaces, which, under various forms, are employed in many of the processes of chemistry as well as in the chemical arts, to excite and apply heat.

The principles on which the production of heat in furnaces depends, are, that inflammable matter cannot burn without the access of air, and that the rapidity of the combustion, and consequently the quantity of heat produced in a given time, are proportional to the quantity of air transmitted over the burning matter. When fuel is placed in a closed cavity, like that of a furnace, connected with a chimney, and kindled, the air is rarefied, and ascends by the chimney ; the pressure of the external atmosphere forces a quantity of fresh air through the openings below, which, rising through the mass of fuel, occasions a strong combustion. The strength of the combustion depends therefore on two circumstances,—the access of atmospheric air from below, and the due height and width of the tube containing the column of heated air. The first is regulated by registers, consisting of apertures, fitted with brass stoppers, or, what is more convenient, a moveable semicircular plate, adapted to one aperture of sufficient size. The second principally contributes to the rapidity of the combustion. When the tube or chimney is lengthened, the difference between the specific gravity of the column of heated air which it contains, and that of the column of external air being greater, a larger quantity of fresh air is constantly forced through the fuel, and a strong

draught, as it is termed, is formed. This is proportional to the height of the chimney, at least to a certain extent; for beyond a certain height, the air cooling, the difference in specific gravity becomes less, and no advantage is gained. The same advantage is obtained, by causing the air which passes into the furnace to pass through a long tube, disposed horizontally, and connected with the ash-pit, rendered as nearly air-tight as possible; as thus a still greater difference is established between the external and internal columns of air in weight. The narrowing the chimney has to a certain extent a similar effect, though if it be rendered too narrow to admit of the free exit of the air, and the smoke, the current will be impeded. Notwithstanding the importance of these circumstances, the due proportions of height and width of the chimney to the cavity of the furnace have not been well ascertained. Macquer states that the diameter of the chimney ought to be to that of the furnace as 2 to 3 nearly; and that when the internal diameter of the furnace is 12 or 15 inches, if the diameter of the chimney be 8 or 9, and its height 18 or 20 feet, a very intense heat is excited*.

Another important object is the confining the heat or preventing its dissipation. This is accomplished by coating the internal surface with a substance which transmits heat slowly, as a lute of clay and sand, which likewise serves to defend the sides of the furnace, when they are of metal, from the action of the fire. When it is built of brick, the building is a sufficiently imperfect conductor to confine the heat.

* It is often an object of importance to consume the smoke from furnaces, those especially on a large scale employed in manufactures, or those of steam engines, when they are in situations where the smoke proves offensive. A very good summary of the methods that have been employed for this purpose is given in a Report, *Annales de Chimie*, t. 69. p. 189.

A general furnace, applicable to most of the operations of chemistry, contrived by Dr Black, is represented Plate V. Fig. 54. A is the body of an elliptical form, which contains the fuel, and frequently the substance to be operated on ; it is made of plate-iron, and lined to the thickness of two or three inches, first with a mixture of clay and charcoal, beat into a paste with water, and over this, with a coating of clay and sand, the coating being thicker towards the bottom, so as to diminish the cavity, and render it slanting downwards from the chimney. On the top is fixed an iron-plate, having two apertures, one, *a*, placed over the cavity, and designed to receive an iron pot with sand, when evaporation, distillation, or any similar process is to be performed ; the other smaller, to which the chimney B, made of a tube of iron, is fixed. C represents the grate, in a plate of iron which is fixed to the bottom of the body of the furnace, nearly, but not exactly opposite to the larger aperture in the upper plate. D is the ash-pit, the body of the furnace resting within it on a strong ring which runs round the cavity, at about half an inch deep. In this ash-pit is a door, *b*, turning on hinges, to remove the ashes ; and a register, *c*, designed to regulate the admission of air : it is a plate of iron, in which are six apertures, fitted with plugs, the size of which increases in geometrical ratio, so that by opening them singly, or in combination, the supply of air to pass through the fuel, and consequently the heat to be excited, can be regulated with precision. The fuel is introduced at the top, but as it cannot easily be supplied this way in the progress of the process, at least when the sand-pot is used, the furnace is sometimes constructed with a door in the side ; this, however, renders the regulation of the admission of air less perfect. When the furnace is used for fusion, or similar purposes where a sand-pot is not required, the upper aperture is covered with a dome.

Furnaces applied to particular purposes, as the assay-

furnace, used in assaying and other operations on the metals, or the reverberatory furnace, in which by a dome the flame is made to reverberate on the substance operated on; are little used by chemists. It is an object of considerable importance, however, to have a furnace capable of exciting a very intense heat, and different kinds of what is named a melting-furnace, or, from the strong blast of air which is forced through it, a wind-furnace, have been proposed.

A convenient portable one was described by Schmeisser, Fig. 55. It is formed of iron-plates, coated with clay and sand; the cavity being about 12 inches in height, and 6 inches wide, having a dome which terminates in a tubular chimney, about 2 inches in diameter. Besides being adapted to excite a very intense heat, it may be applied to various purposes, and is so far a general furnace. For cupellation, a muffle can be introduced at the door, *a*; for distillation in the naked fire, an earthen retort may be placed in it, the neck resting on the aperture *b* beneath the dome; *cc* are apertures in the sides opposite to each other, through which an iron or earthen tube may be passed, so as to be kept at a red heat; *d* is an aperture to which the nozzle of a double bellows may be adapted to excite a violent heat; *e* is the ash-pit door; *f* a moveable register, to regulate the admission of air.

In operations on a larger scale, a fixed furnace of brick is required. Fig. 62. represents a convenient form of this kind. *A* is the cavity of the furnace, terminating by a passage in the chimney *B*. At *C* is an aperture covered with a thick plate of iron, or of fire-brick, through which fuel is introduced. On the grate *D*, is placed a covered crucible, on a pedestal of baked clay, and in the passage of the chimney, at *a*, a muffle may be placed; *E* is the ash-pit, through which the air is admitted.

Small furnaces which may be placed on a table, and which are useful for experiments on a limited scale, have been constructed of the large black lead crucibles or pots.

A furnace of this kind was described by Lewis, which has been so much improved by Mr Aikin, as to be capable of producing a very intense heat *. I have constructed one which I find very convenient, where an inferior heat is required. It consists (Fig. 59.) of a cylinder of plate-iron 8 inches in height and 5 in width, around which is another cylinder of the same height, but wider, so that there is a space of half an inch between them, this open space being closed at the top and bottom by a slip of plate-iron, folded over, and rivetted. By this double cylinder, the heat is more effectually confined without lute. In the inner cylinder, within $2\frac{1}{2}$ inches of the bottom, are rivetted three small projections, on which lies a plate of iron perforated which supports the fuel, and about $1\frac{1}{2}$ inch below this the smaller cylinder is closed by a plate of iron, so that an ash-pit is formed, to which a door is adapted in front. A little above this is represented in front, an aperture to which the nozzle of small bellows may be adapted, to excite a higher heat, when this is required. A kind of tube of iron is rivetted to one side of the outer cylinder, in which a slender iron rod can be inserted, turned at the top into a circular horizontal ring, which may support a matrass or any smaller vessel, and which, by a thumb-screw, can be placed at different heights. There are two apertures near the top, opposite to each other, (one of which is represented in the figure,) through which a tube may pass across the furnace, so as to admit any gas transmitted through it to high temperature. When it is not necessary that the furnace should be open at the top, a dome of plate iron, B, with a chimney, C, is adapted to it, by which the heat is rendered stronger from the greater current of air established through the fuel, and smoke is carried off. And by a door in this, which moves on a hinge, fresh fuel may be introduced, or the neck of a retort placed in the

* Philosophical Magazine, vol. xvii, p. 146.

body of the furnace may pass out. With this furnace many experiments on a small scale are easily performed. Charcoal is the proper fuel for it.

When solid substances are to be exposed to these high heats, crucibles are the usual containing vessels, at least for experimental purposes. The Hessian crucible, as it is named, is of a species of earthen-ware or baked clay, which stands intense heat without fusing, its only disadvantage is being liable to be cracked by any sudden alteration of temperature. The black-lead crucibles, made of plumbago and clay baked, are not liable to this, and are, therefore, often used, especially in fusing metals; from a number of saline substances, however, they suffer corrosion. Both are made narrow at the bottom, that the fused matter may be collected into a small mass, and either triangular, or if round, pinched at the mouth, that the melted matter may be poured out. The usual forms are represented, Fig. 60, 61. When placed in the furnace, a small clay pedestal is placed on the grate, on which the crucible stands, to remove it from the current of cold air; and a cover is adapted to the mouth, to exclude the fuel. Crucibles of platina are sometimes used. Cupels are small cups made of bone-ashes, very porous: they are used in refining the more precious metals, which are not oxidated by heat and air, any oxidable metal combined with them suffering this change, and the vitrified oxide being absorbed by the cupel. They are placed under an arched earthen vessel, open at the end, named a Muffle, Fig. 56, by which, while the fuel is excluded, the air which is necessary in the process is admitted.

In applying a more moderate heat, the medium of sand, forming the Sand Bath, is employed, and glass vessels named Matrasses or Cucurbits are used. The cucurbit is represented, with the capital, Plate IV. Fig. 38, as the apparatus which is used in sublimation. The matrass is re-

presented Fig. 44. ; from being blown thin and equable, it sustains alterations of temperature with less risk of breaking, and from its long neck any vapour which is condensed falls back.

A convenient method of applying heat from combustion, where it is not necessary that it should be very intense, is by the Lamp-furnace. A lamp with a concentric wick, and internal supply of air, on the principle of Argand's, affords a heat easily regulated by means of the elevation or depression of the wick, and the distance at which it may be placed from the body designed to be heated. By an invention of Mr Webster, in which a double concentric wick is used, the heat is rendered more powerful. The lamp is sometimes attached to an iron or brass rod, on which it slides, and to which are also attached rings of different diameters, to support a retort or evaporating basin above the flame, as represented Fig. 58. It is more convenient to have a detached standard, with rings that can be inserted in a socket, which slides on the rod of the standard, and by a thumb-screw can be fixed at any height.

The blow-pipe affords a mode of applying a strong heat at a small point. This instrument is a conical tube, with a very small aperture at its narrow extremity. It is represented Fig. 57. ; when made of brass, it has the advantage, that small moveable nozzles can be adapted to it, having holes of different diameters, to afford a larger or smaller flame. The artists, prefer, however, one of glass, as it is easier to give a glass tube a fine and smooth aperture. By blowing through this tube on the flame of a candle or lamp, in a horizontal direction, it is urged in a conical form ; and at its extremity, or rather at the extremity of the internal blue flame, a heat comparatively intense is excited. To condense the humidity of the expired air, there is a swell at one part of the tube. This instrument is used by the chemist and mineralogist, in as-

certaining the fusibilities of bodies *. A fragment of the substance to be submitted to trial is placed on a piece of charcoal, or in a spoon of silver or platina, and the flame is directed upon it; or if its fusion is to be promoted by the addition of a flux, it is mixed with it in powder. It is also employed by the artists, in enamelling and in working on glass.

The facility of blowing through the blow-pipe, so as to keep up a current of air, is not easily acquired, and it is fatiguing to continue it for any length of time. Different contrivances have been had recourse to, to obviate this inconvenience. The instrument is sometimes connected by a flexible tube with double bellows worked by the foot, by which a strong stream of air is forced through the tube †. It is difficult, however, to render it uniform, and also to construct bellows which shall be air-tight. To obviate this, Mr Hare constructed a hydrostatic blow-pipe, of which he has given a description ‡. Melograni employs two glass globes, connected by their necks; one of which being half filled with water, is placed so that the water shall run into the other, forcing a stream of air through a tube which issues from it, and which is directed on the flame of a candle ||; and when the air has passed from the one their position may be changed. A still better method is that invented by Mr Tilly ¶, in which a tin or copper box has a partition reaching from the top to within an inch of the bottom, the one compartment being air-tight

* Some important observations on its application to mineralogy have been lately given by Gahn (*Annals of Philosophy*, vol. xi,) which will be noticed in the third volume, under the introductory chapter to the history of Mineral Compounds.

† Cronstedt's *Mineralogy* by Magellan, Appendix.

‡ *Philosophical Magazine*, vol. xiv, p. 238.

|| *Nicholson's Journal*, vol. ix, p. 25, and 143.

¶ *Philosophical Magazine*, vol. xliii, p. 280.

at the top : water is put in so as to fill it three-fourths : by a tube perforating the top and passing to within half an inch of the bottom, air is blown in, which rises through the water, displacing it, and causes it to rise into the other compartment : the tube being closed, the pressure of this column of water forces out the air by a tube with a small aperture at the top, the stream of which may be directed on the flame of a lamp ; and as the air is exhausted, a fresh quantity may be blown in. An apparatus, on a similar principle, consisting of a large glass receiver with a stop-cock, inserted in the neck of an Woolfe's bottle, so as to allow water to run in and expel air, has been proposed by Mr Hume. The common gas-holder, Fig. 48, will be more powerful in effecting the same purpose. Still more recently, Mr Brooke applied a condensing syringe so as to force air into a reservoir of copper, from which it is allowed to escape by a tube regulated by a stop-cock, and having a very small aperture. This apparatus, represented fig. 63, affords a very uniform and powerful stream of air †. Lastly, the vapour of spirit of wine has been employed, a little of the spirit being put into a small vessel heated over the flame of a lamp, and the vapour conducted through a curved tube being directed on the flame of a candle, or of a wick placed in a different part of the same tin lamp as that by which the spirit is heated ‡ : The flame, however, is not so equable as that urged by a current of air, and the method is expensive.

All these contrivances excite heat, from combustion, principally by affording a more rapid supply of air. If, instead of common air, that elastic ingredient of the atmosphere, oxygen gas, which more peculiarly supports combustion, be supplied, a still more intense heat will be ex-

* Philosophical Magazine, vol. xlv, p. 1.

† Annals of Philosophy, vol. vii, p. 367.

‡ Nicholson's Journal, vol. iii, p. 1 ; vol. iv, p. 106.

cited. In this way, accordingly, we can raise the highest heat which can be obtained by artificial arrangements.

The usual method is to form a small cavity in a piece of charcoal, which is kindled by directing flame, urged by a blow-pipe, upon it; the substance designed to be operated on is put into the cavity, and a current of oxygen gas is directed on the red hot charcoal, from a tube with a small aperture which communicates with a gazometer containing the gas. A series of experiments were made in this manner by Lavoisier. All the metals were melted, and with the exception of platina were either dissipated in vapour or made to burn. The earths, with the exception of lime, magnesia, and barytes, were fused; and all the compound earthy fossils were either melted or softened, and in general their colours were destroyed. The heat, Lavoisier remarked, is superior to that excited by the concentration of the solar rays by the most powerful burning glass; as in the focus of the great burning glass of Tschirnhausen, platina is either not changed, or after long exposure is only agglutinated, and jasper, and several other fossils, suffer no alteration, while on the burning charcoal, excited by oxygen gas, all these substances are quickly fused *. If the stream of gas be urged on the flame of oil from a lamp, an intense heat is also excited, though inferior to that from burning charcoal. Dr Marcet found the heat from the flame of spirit of wine excited by the gas, so intense, as instantly to melt platina and quartz †.

Ehrman prosecuted Lavoisier's experiments, and appears to have obtained even a more intense heat; as he volatilized platina, and fused barytes and magnesia, lime being the only earth, and indeed the only substance, which was infusible ‡. A series of similar experiments, by a so-

* Mémoires de l'Acad. des Sciences, 1783, p. 563.

† Annals of Philosophy, vol. ii, p. 99.

‡ Essai d'un Art de Fusion.

ciety in London, is related in the eighth volume of the *Philosophical Magazine*.

Another mode of increasing heat by oxygen gas is that of presenting a current of it to a current of hydrogen gas, and kindling the stream of the mixed gas, each gas being allowed to issue from a separate gazometer, and being united in a common metallic tube, of small width and length, and the mixed stream being kindled at the aperture of the tube. The heat is even more intense than that produced by directing oxygen gas on burning charcoal, silice, barytes and strontites having been melted by it, as well as several mineral bodies which resist fusion in the other method. These results were obtained by Mr Hare of Philadelphia, by whom this method, and the apparatus for applying it were invented *. Some additional experiments were given by Mr Silliman †. And more recently, the method has been applied with much effect by means of the blow-pipe of Mr Brooke, Fig. 63; the mixture of the two gases in the due proportion for a perfect combustion, that is, two measures of hydrogen and one measure of oxygen being put into a bladder, which is connected with an aperture at the top of the condensing syringe, the gas is then forced into the reservoir, in a state of condensation, and being allowed to escape at the aperture of the tube, is inflamed. The advantage of this method, independent of its facility, is, that the proportions of the two gases are more accurately adjusted than when they are in separate reservoirs, and the mixture perhaps acts with more strength in its state of condensation. The heat appears, from the extensive series of experiments by Dr Clarke, to exceed ‡ in intensity that obtained by any other arrangement. But

* *Philosophical Magazine*, vol. xiv, p. 301.

† *American Mineralogical Journal*.

‡ *Annals of Philosophy*, vol. viii. and ix.

Journal of Science, vol. ii.

it is attended with much risk of explosion from the flame passing back to the reservoir. To obviate this, various methods have been employed. The risk is less, when a very narrow tube, discharging the gas, is employed. And conformable to a principle pointed out by Sir H. Davy, on which his safety lamp is founded, that flame does not pass through small metallic tubes or apertures so as to communicate explosion, additional security has been given by interposing a sufficient number of folds of fine metallic wire sieve in the passage between the reservoir and the tube; or by transmitting the gas in part of the passage through a bundle of capillary tubes. Another method has been, to interpose between the reservoir and the discharging tube a small cylindrical chamber half filled with water, or what has been found preferable, with oil, through which the gas is made to pass, so that if an explosion takes place, it extends only to the surface of the fluid. Yet even with this arrangement explosions have occurred, the fluid being liable to be thrown backwards into the reservoir. A screen, therefore, has been used, interposed between the apparatus and the operator, the tube conveying the gas passing through it, and it is prudent to employ always this precaution. The apparatus, in any form, can scarcely, however, be applied to any important practical use, and is only adapted to determine the fusibility of refractory substances*.

Having described the means of producing augmentation of temperature, and their applications to practical chemistry, I have, lastly, to state the methods employed to reduce temperature, or produce cold. These are Rarefaction, Evaporation, and Chemical action.

I have already stated, that when by the removal of pressure, a gas is suddenly rarefied, its temperature is redu-

* *Annals of Philosophy*, vol. ix, x, xi.

Journal of Science, vol. i. and ii.

ced. This is apparent, even in the comparatively slow rarefaction of air in working the air-pump, a thermometer in the receiver sinking, as Dr Cullen long ago remarked, two or three degrees. Darwin observed, that a thermometer placed in the stream of condensed air, expanding as it issues from the receiver of an air-gun, sinks 5 or 7 degrees. The striking phenomena observed in the fountain of Hiero, constructed at the mines of Chemnitz, in Hungary, afford the best example of the production of cold, by rarefaction. In this engine, the air in a large vessel is compressed by a column of water, 260 feet in height; on opening a stop-cock, it rushes out with great violence, and in expanding, the watery vapour which existed in it, is not only deposited, but is congealed, falling like snow, or adhering in icicles to the aperture of the stop-cock *.

The production of cold from evaporable fluids exposed to the atmosphere had been noticed by Mairan and by Wilcke, but was made first the subject of accurate experiment, and ascribed to the evaporation of the fluid, by Dr Cullen. He observed, that a thermometer, when its bulb was immersed in spirit of wine, sunk several degrees on suspending it in the air, but recovered its temperature when it had become dry. With other liquids the same phenomenon was observed, though not to the same extent: with water it was less, and with ether greater †. Hence, as he remarked, the cold produced is greater as the fluid is more evaporable. He found, too, that it is increased by whatever accelerates the evaporation, as by a current of air directed on the wet bulb. If it be wet with water, and the evaporation promoted by blowing a current of air on it, the temperature sinks about 5 degrees of Fahrenheit; if with alkohol, it falls 12 degrees; and from sulphuric ether the fall is above 30 degrees. If the ether

* Philosophical Transactions, vol. lxxviii, p. 43.

† Edinburgh Physical and Literary Essays, vol. ii, p. 159.

be evaporated, therefore, from a small tube containing water, the water will be frozen by the cold produced. If a piece of linen be wrapt round the bulb of a thermometer, be moistened with rectified ether, and exposed to a current of air, the temperature sinks from 50° to 5° . Alcohol applied in the same way sinks it to 31° , and water to 38° *. The evaporation being more rapid when the liquid is placed in a jar on the plate of the air-pump, and the air exhausted, greater cold is produced; and in this way also, as Dr Cullen observed, water may be frozen by the evaporation of ether, by placing a second receiver over the one in which the exhaustion was performed, so as to exclude the heating agency of the atmosphere. Dr Higgins states, that, from the evaporation of ether in this manner, in frosty weather, the temperature is reduced 40° below 32° †. And Dr Marcet has found, that quicksilver may be frozen by it.

An arrangement, by which the cold from evaporation is increased, has been ingeniously contrived by Mr Leslie ‡. When the evaporation of a fluid is accelerated by placing it *in vacuo*, the vapour which is formed from it acts by its elastic force in retarding the progress of the evaporation, and it is laborious and difficult by continued exhaustion to remove this. Mr Leslie obviates the difficulty by introducing the action of a substance which is powerful in absorbing the vapour, placing, for example, a capsule containing water on a standard on the plate of the air-pump, and beneath it a shallow vessel containing sulphuric acid or muriate of lime. Either of these absorbs the vapour as quickly as it is formed, and keeps up a vacuum. Hence the evaporation proceeds with rapidity, and the degree of cold produced in consequence is

* Walker on Cold, p. 82.

† Minutes of a Society for Philosophical Experiments, p. 81.

‡ On the Relations of Air to Heat and Moisture, p. 140.

soon sufficient to cause the water to freeze,—thus producing the result, rather singular, of a fluid being frozen by the cold produced by its own evaporation. Mr Leslie has found, that other substances, still more convenient, may be employed to condense the vapour; such, for example, as the calcined powder of basalt or green-stone: And he has supposed, that the method may be economically practised to form ice on a large scale. And by other arrangements, the intensity of the cold may be increased: by coating, for example, the bulb of a mercurial thermometer with ice, and suspending it, exposed in a similar manner to the action of sulphuric acid in the vacuum of a powerful air-pump, he succeeded in freezing the quicksilver in the bulb, the cold being rendered so intense by the rapid evaporation of the ice, attended, of course, with a still greater augmentation of capacity than attends the transition of water into vapour. Dr Wollaston has introduced a variation in the experiment, in an instrument which he has named the Cryophorus, consisting of two glass balls, connected by a glass tube eight or ten inches in length, bent at right angles at both extremities an inch or two above each ball. A portion of water is put into the balls sufficient to fill one of them about one-half; it is made to boil so as to expel the atmospheric air by an aperture in the tube: this aperture is then hermetically sealed; the included water is collected in one ball, the other ball is surrounded by a freezing mixture, the cold of which condenses the vapour it contains, and continues to condense the fresh quantity of vapour formed, so as to cause the evaporation to proceed with a rapidity sufficient to produce a degree of cold adequate to the freezing of the water*.

Degrees of cold more intense are obtained by the chemical action of certain substances on each other. In such cases, the cold is produced by the mutual action either of

* Philosophical Transactions, 1813.

two solid bodies, or of a solid and a fluid, which in the progress of that action pass into the liquid state; and to this change of form the absorption of caloric, which causes the reduction of temperature, is owing.

The principal ingredients of these Freezing Mixtures as they are named, are substances belonging to the class of salts. Many salts, while dissolving in water, produce considerable cold. By adding nitre to water, in as large a quantity as can be dissolved, the temperature is reduced 17 degrees; and by dissolving muriate of ammonia in water, in the same way, 26 or 28 degrees: Nitrate of ammonia in fine powder, added to an equal weight of water, in dissolving, reduces the temperature from 50° of Fahrenheit to 4° : and 3 parts of muriate of lime, added to 2 of water, sink it from 36° to -1° .

As water, although saturated with one salt, will dissolve a portion of a second, and even of a third, it is possible, by adding two or more salts to water, to obtain a greater cold than from the solution of one. Mr Walker, to whom this had occurred, produced, by mixtures of this kind, degrees of cold which were formerly not obtained without the assistance of ice.

One of the most convenient of these mixtures is composed of equal parts of muriate of ammonia and nitre reduced to powder. Five parts of this mixture, added to eight parts of water at 50° , reduce the temperature to 11° . And what renders it economical is, that by evaporation of the solution, the dry mass obtained answers equally as before, and in this way, when recovered for the twelfth time, had the same effect *. Six parts of nitrate of ammonia, and six of carbonate of soda, added to six of water, reduce the temperature from 50° to -7° , which is the greatest cold obtained from adding salts to water.

When salts are dissolved in acids more or less diluted,

* Walker on the Production of Artificial Cold, p. 25.

still more intense colds are produced, owing to the solution proceeding more rapidly. Sulphate of soda, added to nitrous acid diluted with 1 part of water, gives a fall of temperature from 51° to -1° ; added to sulphuric acid diluted with an equal weight of water, the reduction is from 50° to 5° ; and three parts of the salt in fine powder, with two parts of muriatic acid, reduce the temperature from 50° to 0. When mixed salts are used, the degrees of cold are rather greater. Phosphate of soda 9 parts, nitrate of ammonia 6 parts, and diluted nitric acid 4 parts, form the most powerful of these mixtures, and cause the thermometer to descend from 50° to -21° . By a successive application of these mixtures of salts with acids, so as to reduce the temperature of the materials, Mr Walker succeeded in freezing quicksilver *.

It has been long known, that ice or snow, added to acids, dissolves quickly, and during its solution produces considerable cold. An observation of this kind was made by Boyle, though not much attended to. Experiments on the powers of the different acids were afterwards made by different chemists: and by the cold thus produced, Braun first succeeded in freezing quicksilver, the experiment having been made at Petersburg when the temperature of the atmosphere was low †. The cold varies according to the acid employed, and its state of concentration. According to Lowitz, when the acids are undiluted, muriatic acid produces the greatest cold, nitrous next, and sulphuric acid gives the least; the first, sinking the temperature from the freezing point of water to -29° of Fahrenheit, the second to -22° , and the third to -11° ‡. When diluted, however, the sulphuric acid exceeds the other, a degree of cold equal to -78° having been produ-

* Walker on Cold, p. 35.

† Philosophical Transactions, vol. lii, p. 156.

‡ Annales de Chimie, tom. xii, p. 301.

ced from its action on snow at a very low natural temperature.

From the mutual action of snow or ice, and solid salts, great reductions of temperature are also produced. The experiments of Fahrenheit, in which he obtained the degree of cold at which he commenced the scale of his thermometer, by mixing snow with sea-salt, or with muriate of ammonia, have been long known. Lowitz has more particularly attended to this variety of freezing mixture. The temperature of the atmosphere being 32° of Fahrenheit, a mixture of dry potash with snow, he found, reduced the temperature to -53° . A similar mixture with soda gave a cold of only -15° . Other saline substances gave similar low temperatures, particularly nitrate of lime, muriate of magnesia, muriate of iron, and acetate of potash *; but these were all inferior in producing cold, to the potash. Muriate of lime, however, he found to be still more powerful. The degree of cold produced varies according to the proportions; but the greatest was with 4 parts of the salt and 3 of snow, which sink the temperature from 5° to -56° †. Quicksilver congealing at -40° ; its congelation can be easily obtained by this mixture.

These experiments have been often repeated; and the effects of these intense colds, on a number of substances, have been ascertained. By mixtures of diluted acids with snow, and of muriate of lime with snow, Fourcroy and Vauquelin produced reductions of temperature to 50° , 60° , and even to 65° below the commencement of Fahrenheit's scale. A saturated solution of ammonia in water crystallized at -44° , and at -56 was converted into a semi-transparent mass, and lost nearly all its odour; nitrous acid crystallized at the latter temperature; at -48° sulphuric ether became thick and milky, and at length formed a

* Annales de Chimie tom. xxii, p. 302—3, 305.

† Ibid.

white mass, composed of small crystals ; alkohol could not be congealed *. Guyton, by transmitting ammonia in its gaseous form, and deprived as much as possible of water, into a balloon, cooled by a mixture of muriate of lime and snow, found it condensed into a liquid at -48° of the centigrade scale, or -56° of Fahrenheit †.

In conducting the process of artificial refrigeration, a number of circumstances require to be attended to, in some measure varied according to the kind of freezing mixture which is used. In obtaining cold from the solutions of salts in water, or in acids, it is necessary that the salts should be fresh crystallized, neither efflorescent nor humid, and reduced to fine powder ; the materials ought to be quickly and thoroughly mixed ; the vessel should be just large enough to contain the mixture ; and the vessel in which the substance to be subjected to refrigeration is contained, ought to be of glass, and thin. In employing mixtures of snow with acids or salts, the snow should be loose, dry, and if possible newly fallen ; the quantities of materials should be mixed at once in the due proportion, and as quickly as possible. If muriate of lime be employed, it should be dry, and in fine powder. Lowitz directs that it should be in that state in which it is crystallized with the largest quantity of water of crystallization, by putting its solution to cool, when of the density of 1.5 or 1.53, an observation confirmed by Walker. In cooling the materials, where this is requisite, they ought to be put into separate glass or tin vessels, placed in a freezing mixture of the requisite power ; but care must be taken not to cool them beyond that point at which they act on each other, or, in other words, near to that at which the liquid resulting from their mutual action congeals. Thus, if snow and salt are mixed at -10° of Fahrenheit, they exert no mu-

* *Annales de Chimie*, t. xxix, p. 281.

† *Ibid.* p. 297.

tual action ; or if snow and potash be mixed, each at -69° , they remain solid ; but if the temperature be raised to -53° , their action commences, and a cold is produced of -70° . Lastly, the due proportions of the ingredients should be observed ; for any considerable excess of either, merely communicates caloric to the mixture during the refrigeration, and so far diminishes the effect.

The cold produced by all these mixtures is to be ascribed to the absorption of caloric, which attends the rapid liquefaction of the materials from their chemical action, and is ultimately to be referred to the enlargement of capacity consequent on that change of form ; the cold produced being greater as the capacity is more enlarged. This view was presented by Dr Irvine *. Although it is the ultimate principle of the theory, there are some intermediate facts, which, for its full illustration, require to be stated.

Thus, we may in some measure predict, what substances are best fitted, by their mutual action, to produce cold, —what degree of cold may be expected, from their mixture in any given case,—what will be the maximum of refrigeration,—and what will be the best proportions of the materials to obtain that maximum.

It is obvious, that those substances will produce the greatest cold, which, by mutual action, produce the most rapid solution,—which, during that solution, suffer the greatest augmentation of capacity,—and which form a solution that at low temperatures remains liquid. There is perhaps no individual mixture in which all these circumstances are present to the greatest extent ; yet the knowledge of them enables us to point out the respective powers of the different mixtures which are employed.

Thus, in the solution of a salt in water, there is merely the gradual transition of the solid to the fluid form ; hence

* Essays on Chemical Subjects, p. 18:

the cold produced is not considerable. When two salts are mingled together, these, by their reciprocal action, both accelerate the solution of each other, and enable a given quantity of water to dissolve a greater quantity ; as more solid matter, therefore, passes to the fluid state, and passes more quickly, a greater portion of caloric is absorbed, and a greater degree of cold is produced. The attraction of acids to water, or, to state it more correctly, to the solid matter of water, is strong, and their mutual action is energetic ; ice too is a substance which, in its transition to fluidity, suffers a very considerable augmentation of capacity ; hence it may be concluded, what experiment proves to be just, that from the action of acids on snow or ice, a great degree of cold will arise. Lastly, in the mixture of two solid substances, which by mutual action pass to fluidity, the enlargement of capacity must be greater, and a greater diminution of temperature produced. It is so in fact ; at the same time there is a limit placed to it, from two solids acting with greater slowness than a solid and fluid do ; the transition to fluidity is therefore more gradual, and the caloric not so rapidly absorbed. Hence the cold which is produced in these cases, is not equal, as Blagden observed, to the cold arising from the solution of the salt in water, added to the cold that would also arise from the sudden liquefaction of the ice. This is the reason why mixtures of acids with snow or ice are often equal to the mixtures with solid salts ; because, although in the latter case more matter passes to the fluid form, in the former a given quantity is liquefied more rapidly. And those salts which produce the greatest cold are those which exert the strongest attraction to water, and act on it most rapidly, as potash and muriate of lime.

There is another principle to be attended to, which in these mixtures modifies the quantity of caloric absorbed from the liquefaction. Although the indirect consequence of the chemical action between the substances mixed, is

absorption of caloric, in consequence of the liquefaction it occasions, yet its direct tendency is to evolve caloric, by the increase of density which it occasions, independent of change of form. Hence two effects arise from the mutual action of the ingredients of freezing mixtures; evolution of caloric, as the result of the combination, and absorption of caloric, as the result of the liquefaction to which the combination gives rise; and the ultimate effect is compounded of these, so that the actual change of temperature is only the excess of the one over the other.

It may even happen, that the one shall exactly counter-balance the other; of this there is an example in the solution of sulphate of soda in alcohol, which produces neither heat nor cold; or, it may happen, that the heat from condensation shall exceed the cold from liquefaction, as in the solution of potash in water.

The general principle now stated is exemplified in the action of acids on ice, and, as applied to this case, is clearly stated by La Place: "If the mixture of an acid, with a given quantity of water, produce heat, in mixing that acid with the same quantity of ice, it will produce heat or cold, according as the heat which results from its mixture with water is more or less considerable than that which is necessary to melt the ice *."

On this principle many of the facts connected with the operation of freezing mixtures are explained. Thus we perceive why concentrated sulphuric acid poured on snow or ice produces at first heat instead of cold; the action is so energetic that the caloric evolved from the combination is superior to what is absorbed by the liquefaction. But when the acid is combined with a portion of water, its affinity being thus weakened, its action is less energetic, and less augmentation of temperature attends their union. Hence in the progress of the experiment in which the con-

* Mémoires de l'Acad. des Sciences, 1780, p. 392.

centrated acid is poured on snow, although heat is at first produced, it is soon succeeded by cold; or if the acid has been previously diluted with a portion of water, it will, when added to the snow, immediately produce cold. Even nitric acid, as Cavendish observed, produces at first a degree of heat when added to snow, but when diluted with $\frac{1}{4}$ th of water, it *immediately* occasions cold. The requisite dilution is, therefore, less in nitric than it is in sulphuric acid, and it is still less in muriatic; and we perceive the reason of this,—these acids evolving less caloric when they combine with water than sulphuric acid does, and, therefore, counteracting less the cold from the liquefaction. And, lastly, if the dilution of the acid be carried too far, its attraction may be so much weakened, that its action on the snow will be feeble, the liquefaction will be performed slowly, and no great cold will be occasioned.

In the other kind of freezing mixtures, there can be no doubt that the same circumstance operates. The heat from combination always counteracts the cold from liquefaction; it is only the excess that prevails, and in no case is the whole reduction of temperature that would arise from the liquefaction of the quantity of matter employed, obtained. This explains the fact, that crystallized salts produce more cold than the same salts deprived of their water of crystallization; as by its presence, the mutual action of the salt and the substance mixed with it is rendered less energetic, and therefore less heat is evolved from the combination; and probably water, in becoming liquid, suffers a greater enlargement of capacity than a salt does; which will increase the refrigerating power of the crystallized salts.

From these observations, it follows, that the greatest cold will be from the mutual action of substances which pass most quickly into the fluid state, and which in that transition have their capacities most enlarged. But as this rapid action is the result of an energetic affinity, this may

counteract, by the evolution of caloric to which it gives rise, the cold that would be produced. In all cases, therefore, there will be a certain state of concentration of the materials, and a certain proportion of them, from which the greatest cold will be obtained.

It may be remarked, too, that we do not obtain the reduction of temperature to the lowest point in the thermometrical scale from those mixtures which, during their mutual action, absorb most caloric. If we take two freezing mixtures at 32° , the one, for example, muriate of lime and snow, the other diluted sulphuric acid and snow, the former will produce more cold than the latter, it will sink the thermometer to -40° or -50° , while the other will sink it to not more than -25° . But we may reach a lower point in the scale of temperature, by successive applications of diluted sulphuric acid and snow, than we can do by muriate of lime and snow; for, past a certain temperature, the latter mixture does not liquefy, but, on the contrary, were it liquid would become solid, while the former remains liquid at lower temperatures than this. If we cool, previous to mixture, muriate of lime and snow to -73° , no advantage is gained; for they cannot produce a temperature lower than this, as their combination cannot exist liquid below that point; and even by approaching closely to it before mixture, we diminish their mutual action, by adding to the cohesion of each. But by previously cooling diluted sulphuric acid and snow, an important advantage is gained; the same limit is not placed to their mutual action, and the lower the temperature is reduced, it is obvious, that the lower will the temperature be that results from their mutual action, down to the point at which the liquid formed by the action of the acid on the snow congeals.

The cold, therefore, from a freezing mixture, can never exceed that point at which the liquid resulting from that mixture congeals or crystallizes, and must indeed always

be a degree or two above it. A saturated solution of sea-salt in water congeals at a few degrees below 0 of Fahrenheit; and hence the cold resulting from that salt mixed with ice is never lower than this. This gives us the reason why sulphate of soda scarcely produces any cold when mixed with ice, as it lowers the freezing point of water only a few degrees, while potash or muriate of lime produce intense colds, as they lower that point to a much greater extent. It also, in some measure, determines the proportions in which the substances should be mixed; those being best, in which the action shall be most rapid, without being too energetic to evolve heat from the combination; and in which the resulting solution is of that strength that is least liable to congeal or crystallize. A little sea-salt added to water depresses its freezing point only a few degrees; and therefore, to add a small portion of it to snow, cannot produce much cold; while, when added until the water is saturated, that is in the proportion of 1 of salt to $2\frac{1}{2}$ of snow, the freezing point is lowered to -6° ; and therefore, by adding it in that proportion to snow, nearly that temperature is attained.

A table of the different freezing mixtures, with their powers in reducing temperature, is inserted, with the other tables connected with the subject of caloric, concluding this chapter.

TABLES CONNECTED WITH THE RELATIONS OF CALORIC,
REFERRED TO IN THE PRECEDING SECTIONS.

TABLES OF CORRESPONDENCE OF THE DIFFERENT THERMOMETRIC
SCALES, REFERRED TO PAGE 215.

TABLE FOR REAUMUR'S THERMOMETER.

Reau.	Cent.	Fahr.	Reau.	Cent.	Fahr.	Reau.	Cent.	Fahr.
80	100.	212.	42	52.5	126.5	4	5.	41.
79	98.75	209.75	41	51.25	124.25	3	3.75	38.75
78	97.5	207.5	40	50.	122.	2	2.5	36.5
77	96.25	205.25	39	48.75	119.75	1	1.25	34.25
76	95.	203.	38	47.5	117.5	0	0	32.
75	93.75	200.75	37	46.25	115.25	-1	-1.25	29.75
74	92.5	198.5	36	45.	113.	-2	-2.5	27.5
73	91.25	196.25	35	43.75	110.75	-3	-3.75	25.25
72	90.	194.	34	42.5	108.5	-4	-5.	23.
71	88.75	191.75	33	41.25	106.25	-5	-6.25	20.75
70	87.5	189.5	32	40.	104.	-6	-7.5	18.5
69	86.25	187.25	31	38.75	101.75	-7	-8.75	16.25
68	85.	185.	30	37.5	99.5	-8	-10.	14.
67	83.75	182.75	29	36.25	97.25	-9	-11.25	11.75
66	82.5	180.5	28	35.	95.	-10	-12.5	9.5
65	81.25	178.25	27	33.75	92.75	-11	-13.75	7.25
64	80.	76.	26	32.5	90.5	-12	-15.	5.
63	78.75	173.75	25	31.25	88.25	-13	-16.25	2.75
62	77.5	171.5	24	30.	86.	-14	-17.5	0.5
61	76.25	169.25	23	28.75	83.75	-15	-18.75	-1.75
60	75.	167.	22	27.5	81.5	-16	-20.	-4.
59	73.75	164.75	21	26.25	79.25	-17	-21.25	-6.25
58	72.5	162.5	20	25.	77.	-18	-22.5	-8.5
57	71.25	160.25	19	23.75	74.75	-19	-23.75	-10.75
56	70.	158.	18	22.5	72.5	-20	-25.	-13.
55	68.75	155.75	17	21.25	70.25	-21	-26.25	-15.25
54	67.5	153.5	16	20.	68.	-22	-27.5	-17.5
53	66.25	151.25	15	18.75	65.75	-23	-28.75	-19.75
52	65.	149.	14	17.5	63.5	-24	-30.	-22.
51	63.75	146.75	13	16.25	61.25	-25	-31.25	-24.25
50	62.5	144.5	12	15.	59.	-26	-32.5	-26.5
49	61.25	142.25	11	13.75	56.75	-27	-33.75	-28.75
48	60.	140.	10	12.5	54.5	-28	-35.	-31.
47	58.75	137.75	9	11.25	52.25	-29	-36.25	-33.25
46	57.5	135.5	8	10.	50.	-30	-37.5	-35.5
45	56.25	133.25	7	8.75	47.75	-31	-38.75	-37.75
44	55.	131.	6	7.5	45.5	-32	-40.	-40.
43	53.75	128.75	5	6.25	43.25	-33	-41.25	-42.25

TABLE FOR THE CENTIGRADE THERMOMETER.

<i>Cent.</i>	<i>Reau.</i>	<i>Fahr.</i>	<i>Cent.</i>	<i>Reau.</i>	<i>Fahr.</i>	<i>Cent.</i>	<i>Reau.</i>	<i>Fahr.</i>
100	80.	212.	53	42.4	127.4	6	4.8	42.8
99	79.2	210.2	52	41.6	125.6	5	4.	41.
98	78.4	208.4	51	40.8	123.8	4	3.2	39.2
97	77.6	206.6	50	40.	122.	3	2.4	37.4
96	76.8	204.8	49	39.2	120.2	2	1.6	35.6
95	76.	203.	48	38.4	118.4	1	0.8	33.8
94	75.2	201.2	47	37.6	116.6	0	0.	32.
93	74.4	199.4	46	36.8	114.8	-1	-0.8	30.2
92	73.6	197.6	45	36.	113.	-2	-1.6	28.4
91	72.8	195.8	44	35.2	111.2	-3	-2.4	26.6
90	72.	194.	43	34.4	109.4	-4	-3.2	24.8
89	71.2	192.2	42	33.6	107.6	-5	-4.	23.
88	70.4	190.4	41	32.8	105.8	-6	-4.8	21.2
87	69.6	188.6	40	32.	104.	-7	-5.6	19.4
86	68.8	186.8	39	31.2	102.2	-8	-6.4	17.6
85	68.	185.	38	30.4	100.4	-9	-7.2	15.8
84	67.2	183.2	37	29.6	98.6	-10	-8.	14.
83	66.4	181.4	36	28.8	96.8	-11	-8.8	12.2
82	65.6	179.6	35	28.	95.	-12	-9.6	10.4
81	64.8	177.8	34	27.2	93.2	-13	-10.4	8.6
80	64.	176.	33	26.4	91.4	-14	-11.2	6.8
79	63.2	174.2	32	25.6	89.6	-15	-12.	5.
78	62.4	172.4	31	24.8	87.8	-16	-12.8	3.2
77	61.6	170.6	30	24.	86	-17	-13.6	1.4
76	60.8	168.8	29	23.2	84.2	-18	-14.4	-0.4
75	60.	167.	28	22.4	82.4	-19	-15.2	-2.2
74	59.2	165.2	27	21.6	80.6	-20	-16.	-4.
73	58.4	163.4	26	20.8	78.8	-21	-16.8	-5.8
72	57.6	161.6	25	20.	77.	-22	-17.6	-7.6
71	56.8	159.8	24	19.2	75.2	-23	-18.4	-9.4
70	56.	158.	23	18.4	73.4	-24	-19.2	-11.2
69	55.2	156.2	22	17.6	71.6	-25	-20.	-13.
68	54.4	154.4	21	16.8	69.8	-26	-20.8	-14.8
67	53.6	152.6	20	16.	68.	-27	-21.6	-16.6
66	52.8	150.8	19	15.2	66.2	-28	-22.4	-18.4
65	52.	149.	18	14.4	64.4	-29	-23.	-20.2
64	51.2	147.2	17	13.6	62.6	-30	-24.2	-22.
63	50.4	145.4	16	12.8	60.8	-31	-24.2	-23.8
62	49.6	143.6	15	12.	59.	-32	-25.	-25.6
61	48.8	141.8	14	11.2	57.2	-33	-26.8	-27.4
60	48.	140.	13	10.4	55.4	-34	-27.	-29.2
59	47.2	138.2	12	9.6	53.6	-35	-28.	-31.
58	46.4	136.4	11	8.8	51.8	-36	-28.	-32.8
57	45.6	134.6	10	8.	50.	-37	-28.	-34.6
56	44.8	132.8	9	7.4	48.4	-38	-30.	-36.4
55	44.	131.	8	6.2	46.2	-39	-31.	-38.
54	43.2	129.2	7	5.	44.6	-40	-32.	-40.

TABLE FOR FAHRENHEIT'S THERMOMETER.

<i>Fahr.</i>	<i>Reau.</i>	<i>Cent.</i>	<i>Fahr.</i>	<i>Reau.</i>	<i>Cent.</i>	<i>Fahr.</i>	<i>Reau.</i>	<i>Cent.</i>
212	80.00	100.00	170	61.55	76.66	128	42.66	55.3
211	79.55	99.44	169	60.88	76.11	127	42.22	52.77
210	79.11	98.88	168	60.44	75.55	126	41.77	52.22
209	78.66	98.33	167	60.00	75.00	125	41.33	51.66
208	78.22	97.77	166	59.55	74.44	124	40.88	51.11
207	77.77	97.22	165	59.11	73.88	123	40.44	50.55
206	77.33	96.66	164	58.66	73.33	122	40.00	50.00
205	76.88	96.11	163	58.22	72.22	121	39.55	49.44
204	76.44	95.55	162	57.77	72.77	120	39.11	48.88
203	76.00	95.00	161	57.33	71.66	119	38.66	48.33
202	75.55	94.44	160	56.88	71.11	118	38.22	48.77
201	75.11	93.88	159	56.44	70.55	117	37.77	47.22
200	74.66	93.33	158	56.00	70.00	116	37.33	46.66
199	74.22	92.77	157	55.55	69.44	115	36.88	46.11
198	73.77	92.22	156	55.11	68.88	114	36.44	45.55
197	73.33	91.66	155	54.66	68.33	113	36.00	45.00
196	72.88	91.11	154	54.22	67.77	112	35.55	44.44
195	72.44	90.55	153	53.77	67.22	111	35.11	43.88
194	72.00	90.00	152	53.33	66.66	110	34.66	43.33
193	71.55	89.44	151	52.88	66.11	109	34.22	42.77
192	71.11	88.88	150	52.44	65.55	108	33.77	42.22
191	70.66	88.33	149	52.00	65.00	107	33.33	41.66
190	70.22	87.77	148	51.55	64.44	106	32.88	41.11
189	69.77	87.22	147	51.11	63.88	105	32.44	40.55
188	69.33	86.66	146	50.66	63.33	104	32.00	40.00
187	68.88	86.11	145	50.22	62.77	103	31.55	39.44
186	68.44	85.55	144	49.77	62.22	102	31.11	38.88
185	68.00	85.00	143	49.33	61.66	101	30.66	38.33
184	67.55	84.44	142	48.88	61.11	100	30.22	37.77
183	67.11	83.88	141	48.44	60.55	99	29.77	37.22
182	66.66	83.33	140	48.00	60.00	98	29.33	36.66
181	66.22	82.77	139	47.55	59.44	97	28.88	36.11
180	65.77	82.22	138	47.11	58.88	96	28.44	35.55
179	65.33	81.66	137	46.66	58.33	95	28.00	35.00
178	64.88	81.11	136	46.22	57.77	94	27.55	34.44
177	64.44	80.55	135	45.77	57.22	93	27.11	33.88
176	64.00	80.00	134	45.33	56.66	92	26.66	33.33
175	63.55	79.44	133	44.88	56.11	91	26.22	32.77
174	62.11	78.88	132	44.55	55.55	90	25.27	32.22
173	62.66	78.33	131	44.00	55.00	89	25.33	31.66
172	62.22	77.77	130	43.55	54.44	88	24.88	31.11
171	61.77	77.22	129	43.11	53.88	87	24.44	30.55

TABLE FOR FAHRENHEIT'S THERMOMETER.

<i>Fahr.</i>	<i>Reau.</i>	<i>Cent.</i>	<i>Fahr.</i>	<i>Reau.</i>	<i>Cent.</i>	<i>Fahr.</i>	<i>Reau.</i>	<i>Cent.</i>
86	24.00	50.00	43	4.88	6.11	0	-14.22	-17.77
85	23.55	29.44	42	4.44	5.55	-1	-14.66	-18.53
84	23.11	28.88	41	4.00	5.00	-2	-15.11	-18.88
83	22.66	28.55	40	3.55	4.44	-3	-15.55	-19.44
82	22.22	27.77	39	3.11	3.88	-4	-16.00	-20.00
81	21.77	27.22	38	2.66	3.33	-5	-16.44	-20.55
80	21.33	26.66	37	2.22	2.77	-6	-16.88	-21.11
79	20.88	26.11	36	1.77	2.22	-7	-17.33	-21.66
78	20.44	25.55	35	1.33	1.66	-8	-17.77	-22.22
77	20.00	25.00	34	0.88	1.11	-9	-18.22	-22.77
76	19.55	24.44	33	0.44	0.55	-10	-18.66	-23.33
75	19.11	23.88	32	0.	0.	-11	-19.11	-23.88
74	18.66	23.33	31	-0.44	-0.55	-12	-19.55	-24.44
73	18.22	22.77	30	-0.88	-1.11	-13	-20.00	-25.00
72	17.77	22.22	29	-1.33	-1.66	-14	-20.44	-25.55
71	17.33	21.66	28	-1.77	-2.22	-15	-20.88	-26.11
70	16.88	21.11	27	-2.22	-2.77	-16	-21.33	-26.66
69	16.44	20.55	26	-2.66	-3.33	-17	-21.77	-27.22
68	16.00	20.00	25	-3.11	-3.88	-18	-22.22	-27.77
67	15.55	19.44	24	-3.55	-4.44	-19	-22.66	-28.33
66	15.11	18.88	23	-4.00	-5.00	-20	-23.11	-28.88
65	14.66	18.33	22	-4.44	-5.55	-21	-23.55	-29.44
64	14.22	17.77	21	-4.88	-6.11	-22	-24.00	-30.00
63	13.77	17.22	20	-5.33	-6.66	-23	-24.44	-30.55
62	13.33	16.66	19	-5.77	-7.22	-24	-24.88	-31.11
61	12.88	16.11	18	-6.22	-7.77	-25	-25.33	-31.66
60	12.44	15.55	17	-6.66	-8.33	-26	-25.77	-32.22
59	12.00	15.00	16	-7.11	-8.88	-27	-26.22	-32.77
58	11.55	14.44	15	-7.55	-9.44	-28	-26.66	-33.33
57	11.11	13.88	14	-8.00	-10.00	-29	-27.11	-33.88
56	10.66	13.33	13	-8.44	-10.55	-30	-27.55	-34.44
55	10.22	12.77	12	-8.88	-11.11	-31	-28.00	-35.00
54	9.77	12.22	11	-9.33	-11.66	-32	-28.44	-35.55
53	9.33	11.66	10	-9.77	-12.22	-33	-28.88	-36.11
52	8.88	11.11	9	-10.22	-12.77	-34	-29.33	-36.66
51	8.44	10.55	8	-10.66	-13.33	-35	-29.77	-37.22
50	8.00	10.00	7	-11.11	-13.88	-36	-30.22	-37.77
49	7.55	9.44	6	-11.55	-14.44	-37	-30.66	-38.33
48	7.11	8.88	5	-12.00	-15.00	-38	-31.11	-38.88
47	6.66	8.33	4	-12.44	-15.55	-39	-31.55	-39.44
46	6.22	7.77	3	-12.88	-16.11	-40	-32.00	-40.00
45	5.77	7.22	2	-13.33	-16.66			
44	5.33	6.66	1	-13.77	-17.22			

TABLES OF THE EXPANSIONS OF SOLIDS FROM HEAT,
REFERRED TO PAGE 237.

The expansions of a number of solids, it is remarked in the text, have been determined by Smeaton, Roy, and Troughton. To these Gay-Lussac has lately added the results of a series of experiments by Lavoisier and La Place, which had not been before published. (*Annales de Chimie et Physique*, t. 1.) He has also reduced the whole to the expansion in the same interval of temperature, that from freezing to boiling water, and has represented it in a similar manner. I therefore give his tables, as affording more direct comparative results. The experiments of Smeaton are given in the 47th volume, and those of Roy in the 75th volume of the *Philosophical Transactions*.

I. TABLE OF THE LINEAR DILATATION OF DIFFERENT SUBSTANCES FROM THE TEMPERATURE OF FREEZING TO THAT OF BOILING WATER, ACCORDING TO THE EXPERIMENTS OF LAVOISIER AND LA PLACE.

SUBSTANCES.	DILATATION FOR A LENGTH EQUAL TO UNITY.	
	In decimal fractions.	In vulgar fractions.
Steel not tempered, - - -	0,00107915	$\frac{1}{927}$
Steel tempered and annealed at a heat of 150°,	0,00123956	$\frac{1}{807}$
Silver cupelled, - - -	0,00190974	$\frac{1}{524}$
Silver standard of Paris, - - -	0,00190868	$\frac{1}{524}$
Copper, - - -	0,00171733	$\frac{1}{582}$
Brass, - - -	0,00187821	$\frac{1}{532}$
Tin of Malacca, - - -	0,00195765	$\frac{1}{513}$
Tin of Cornwall, - - -	0,00217298	$\frac{1}{462}$
Iron forged, - - -	0,00122045	$\frac{1}{818}$
Iron wire, - - -	0,00125604	$\frac{1}{802}$
Flint-glass, English, - - -	0,00081166	$\frac{1}{123}$
Mercury (in volume,) - - -	0,01847746	$\frac{1}{5412}$
Gold, pure, - - -	0,00146606	$\frac{1}{682}$
Gold standard not annealed, - - -	0,00155155	$\frac{1}{645}$
Gold standard annealed, - - -	0,00151361	$\frac{1}{661}$
Platina, - - -	0,00085655	$\frac{1}{1167}$
Lead, - - -	0,00281236	$\frac{1}{354}$
Glass, French, with lead, - - -	0,00087199	$\frac{1}{1147}$
Glass without lead (in tube,) - - -	0,00089694	$\frac{1}{1115}$
Glass mirror, - - -	0,00089089	$\frac{1}{1122}$

II. TABLE ACCORDING TO THE EXPERIMENTS OF SNEATON.

SUBSTANCES.	DILATATION FOR A LENGTH EQUAL TO UNITY.	
	In decimal fractions.	In vulgar fractions.
Blistered steel, - - -	0,00115000	$\frac{1}{870}$
Tempered steel, - - -	0,00122500	$\frac{1}{816}$
Bismuth, - - -	0,00139167	$\frac{1}{719}$
Copper hammered, - - -	0,00170000	$\frac{1}{588}$
Copper 8 parts with 1 of tin, - -	0,00181667	$\frac{1}{550}$
Cast brass, - - -	0,00187500	$\frac{1}{533}$
Brass, 16 parts with 1 of tin, - -	0,00190833	$\frac{1}{524}$
Fine pewter, - - -	0,00228333	$\frac{1}{438}$
Grain tin, - - -	0,00248333	$\frac{1}{403}$
Iron, - - -	0,00125833	$\frac{1}{795}$
Brass wire, - - -	0,00193333	$\frac{1}{517}$
Speculum metal, - - -	0,00193333	$\frac{1}{517}$
Lead, - - -	0,00286667	$\frac{1}{349}$
Antimony, - - -	0,00108333	$\frac{1}{923}$
Lead 2 parts with 1 of tin, - -	0,00250533	$\frac{1}{399}$
Copper 2 parts with 1 of zinc, - -	0,00205833	$\frac{1}{486}$
White glass (barometer tube,) - -	0,00085333	$\frac{1}{1175}$
Zinc, - - -	0,00294167	$\frac{1}{340}$
Zinc hammered, - - -	0,00310833	$\frac{1}{322}$
Zinc 8 parts with 1 of tin, - - -	0,00269167	$\frac{1}{372}$

III. TABLE ACCORDING TO THE EXPERIMENTS OF ROY.

SUBSTANCES.	FOR A LENGTH EQUAL TO UNITY.	
	In decimal fractions.	In vulgar fractions.
Steel rod, - - - -	0,00114450	$\frac{1}{874}$
Brass scale, Hamburg, - - -	0,00185550	$\frac{1}{539}$
Brass plate rod, English, - - -	0,00189296	$\frac{1}{528}$
Brass plate trough, English, - -	0,00189450	$\frac{1}{528}$
Cast iron prism, - - - -	0,00111000	$\frac{1}{901}$
Glass tube, - - - -	0,00077550	$\frac{1}{1299}$
Glass rod, - - - -	0,00080833	$\frac{1}{1237}$

IV. TABLE ACCORDING TO THE EXPERIMENTS OF TROUGHTON.

SUBSTANCES.				LINEAR DILATATIONS FROM THE TEMPERATURE OF FREEZ- ING TO BOILING WATER.
Steel,	-	-	-	$0,0011899 = \frac{1}{848}$
Silver,	-	-	-	$0,0020826 = \frac{1}{480}$
Copper,	-	-	-	$0,0019188 = \frac{1}{521}$
Iron wire,	-	-	-	$0,0014401 = \frac{1}{694}$
Platina,	-	-	-	$0,0009918 = \frac{1}{1008}$
Palladium (according to Wollaston,)	-	-	-	$0,0010 = \frac{1}{1000}$

TABLE OF THE EXPANSIONS OF LIQUIDS.

The expansions in this table were found by Mr Dalton. They are equal to what would be produced by an elevation of temperature from the freezing to the boiling point of water, the volume at the former being 1.

Mercury.....	.0200	$= \frac{1}{50}$
Water.....	.0466	$= \frac{1}{21.5}$
Water saturated with salt.....	.0500	$= \frac{1}{20}$
Sulphuric acid.....	.0600	$= \frac{1}{17}$
Muriatic acid.....	.0600	$= \frac{1}{17}$
Oil of turpentine.....	.0700	$= \frac{1}{14}$
Ether.....	.0700	$= \frac{1}{14}$
Fixed oils...	.0800	$= \frac{1}{12.5}$
Alkohol.....	.0110	$= \frac{1}{9}$
Nitric acid.....	.0110	$= \frac{1}{9}$

TABLE OF CAPACITIES OF BODIES FOR CALORIC.

THE principle on which the tables of the capacities of bodies for caloric are constructed, has been explained in the text, (page 394). These capacities, expressing the quantities of caloric which bodies contain at a given temperature, are entirely comparative, and refer to water as a standard, its capacity being stated at 1.0000. As the capacities of bodies are different, as they exist in the solid, liquid, and aërial state, I have subdivided the following table according to these forms: and I have also placed, in distinct tables, the results obtained by the different modes of experiment that have been employed, as these, according to the observations made in the text, cannot be of equal authority. The first table comprises the results which have been obtained by the mode of mixture, and by the calorimeter, these agreeing in principle, the capacities found by them being inferred from measuring the quantity of caloric given out by a body in suffering a certain change of temperature, by the effect that quantity produces on another body to which it is communicated. Dr Crawford's results form the basis of this table, to which I have added those established by Irvine, Wilcke, Gadolin, Lavoisier and La Place, and Kirwan, (these last having been reported by Magellan as communicated to him by Mr Kirwan,) and also the capacities of some solids ascertained by Mr Dalton by this method. The second table comprises the capacities of bodies estimated from observing their times of cooling, established by the experiments of Leslie and Dalton. The third table denotes the capacities of aërial fluids, ascertained by Berard and Delaroche. The initial letter of the name of each author is annexed to the numbers; and where a difference exists in the capacity of any body as ascertained by different chemists, I have given it according to each, with a reference by numbers, within brackets, so that the authorities may be compared, and that selected on which it may be supposed most reliance is to be placed.

TABLE OF CAPACITIES.—NO. I.

Gases.

1 Hydrogen gas, (178)	-	-	-	21.4000 C.
2 Oxygen gas, (180)	-	-	-	4.7490 —
3 Atmospheric air, (177)	-	-	-	1.7900 —
4 Aqueous vapour, (185)	-	-	-	1.5500 —
5 Carbonic acid gas, (179)	-	-	-	1.0454 —
6 Nitrogen gas, (181)	-	-	-	.7936 —

Liquids.

7 Solution of carbonate of ammonia, (154)	-	-	-	1.8510 K.
8 ——— of brown sugar,	-	-	-	1.0360 —
9 Alcohol, 15, 44, (153)	-	-	-	1.0860 —
10 Arterial blood,	-	-	-	1.0300 C.
11 Water,	-	-	-	1.0000
12 Cows milk, (153)	-	-	-	.9999 C.
13 Sulphuret of ammonia,	-	-	-	.9940 K.
14 Solution of muriate of soda, 1 in 10 of water,	-	-	-	.9360 G.
15 Alcohol, (9, 44, 158)	-	-	-	.9300 Ir.
16 Sulphuric acid, diluted with 10 of water,	-	-	-	.9250 G.
17 Solution of muriate of soda in 6.4 of water,	-	-	-	.9050 —
18 Venous blood,	-	-	-	.8928 C.
19 Sulphuric acid, with 5 parts of water,	-	-	-	.8760 G.
20 Solution of muriate of soda in 5 of water,	-	-	-	.8680 —
21 Nitric acid, (39, 159)	-	-	-	.8440 K.
22 Solution of sulphate of magnesia in 2 of water,	-	-	-	.8440 —
23 ——— muriate of soda in 8 of water,	-	-	-	.8320 —
24 ——— muriate of soda in 3.33 of water,	-	-	-	.8208 G.
25 ——— nitrate of potash in 8 of water,	-	-	-	.8167 L.
26 ——— muriate of soda in 2.8 of water,	-	-	-	.8020 G.
27 ——— muriate of ammonia in 1.5 of water,	-	-	-	.7980 K.
28 ——— muriate of soda saturated. or in 2.69 of water,	-	-	-	.7940 G.
29 ——— supertartrate of potash in 257.5 of water,	-	-	-	.7650 K.
30 ——— carbonate of potash,	-	-	-	.7590 —
31 Colourless sulphuric acid, (51, 55, 56, 57, 175),	-	-	-	.7580 —
32 Sulphuric acid, with 2 parts of water,	-	-	-	.7490 G.
33 Solution of sulphate of iron in 2.5 of water,	-	-	-	.7340 K.
34 Solution of sulphate of soda in 2.9 of water,	-	-	-	.7280 —
35 Olive oil, (172)	-	-	-	.7100 —
36 Water of ammonia, specific gravity, 0.997, (152)	-	-	-	.7080 —
37 Muriatic acid, specific gravity, 1.122, 169)	-	-	-	.6800 —
38 Sulphuric acid. 4 parts with 5 of water,	-	-	-	.6651 L.
39 Nitric acid. specific gravity 1.29895, (21, 159)	-	-	-	.6615 —
40 Solution of alum in 4.45 of water,	-	-	-	.6490 K.
41 Mixture of nitric acid with lime, $9\frac{1}{3}$ to 1,	-	-	-	.6189 L.
42 Sulphuric acid, with an equal weight of water,	-	-	-	.6050 G.
43 ——— 4 parts with 3 of water,	-	-	-	.6031 L.
44 Alcohol, (9, 15, 158, 165)	-	-	-	.6021 C.
45 Nitrous acid, specific gravity 1.354,	-	-	-	.5760 K.
46 Linseed oil,	-	-	-	.5280 —
47 Spermaceti oil, (53, 171)	-	-	-	.5000 C.
48 Sulphuric acid, with $\frac{1}{2}$ of water,	-	-	-	.5000 G.

49	Oil of turpentine, (52)	-	-	-	-	.4720 K.
50	Sulphuric acid, with $\frac{1}{4}$ of water,	-	-	-	-	.4420 G.
51	Sulphuric acid (31, 55, 5, 57, 173)	-	-	-	-	.4390 C.
52	Oil of turpentine, (49)	-	-	-	-	.4000 Ir.
53	Spermaceti oil, (47, 171)	-	-	-	-	.3990 K.
54	Red wine vinegar, (155)	-	-	-	-	.3870 —
55	Sulphuric acid. concentrated and colourless, (31)	-	-	-	-	.3390 G.
56	————— specific gravity 1.87058,	-	-	-	-	.3515 L.
57	————— 31, 51, 174)	-	-	-	-	.3330 Ir.
58	Spermaceti melted,	-	-	-	-	.3200 —
59	Quicksilver specific gravity 13.30, (175)	-	-	-	-	.0530 K.
60	—————	-	-	-	-	.0200 L.
61	—————	-	-	-	-	.0290 W.
62	—————	-	-	-	-	.0280 Ir.

Solids.

63	Ice,	-	-	-	-	.9000 K.
64	—————	-	-	-	-	.8000 Ir.
65	Ox hide, with the hair,	-	-	-	-	.7870 C.
66	Sheep's lungs,	-	-	-	-	.7690 —
67	Beef of an ox,	-	-	-	-	.7400 —
68	Rice,	-	-	-	-	.5060 C.
69	Horse beans,	-	-	-	-	.5020 —
70	Dust of the pine-tree,	-	-	-	-	.5000 —
71	Pease.	-	-	-	-	.4920 —
72	Wheat,	-	-	-	-	.4770 —
73	White wax,	-	-	-	-	.4500 G.
74	Quicklime, with water, in the proportion of 16 to 9,	-	-	-	-	.4391 L.
75	Barley,	-	-	-	-	.4210 C.
76	Oats,	-	-	-	-	.4160 —
77	Charcoal of birch-wood, (86)	-	-	-	-	.3950 G.
78	Carbonate of magnesia,	-	-	-	-	.3790 —
79	Prussian blue,	-	-	-	-	.3300 —
80	Quicklime,	-	-	-	-	.3000 D.
81	————— saturated with water, and dried,	-	-	-	-	.2800 G.
82	Pit-coal,	-	-	-	-	.2800 D.
83	—————	-	-	-	-	.2777 C.
84	Chalk,	-	-	-	-	.2700 D.
85	Artificial gypsum,	-	-	-	-	.2640 G.
86	Charcoal, (77)	-	-	-	-	.2631 C.
87	Chalk, (84, 96)	-	-	-	-	.2564 —
88	Rust of iron,	-	-	-	-	.2500 —
89	White clay,	-	-	-	-	.2410 G.
90	Sea salt, (94)	-	-	-	-	.2300 D.
91	White oxide of antimony washed,	-	-	-	-	.2272 C.
92	Oxide of copper,	-	-	-	-	.2272 —
93	Quicklime, (80, 95)	-	-	-	-	.2229 —
94	Muriate of soda in crystals, (90)	-	-	-	-	.2260 G.
95	Quicklime, (80, 95)	-	-	-	-	.2168 L.
96	Chalk, (84, 97)	-	-	-	-	.2070 G.
97	Crown glass,	-	-	-	-	.2000 Ir.
98	Agate, specific gravity 2618,	-	-	-	-	.1950 W.
99	Earthen-ware,	-	-	-	-	.1950 K.
100	Crystal glass without lead,	-	-	-	-	.1929 L.
101	Cinders,	-	-	-	-	.1923 C.

102	Flint-glass, specific gravity 287, (106)	-	-	.1900 D.
103	Sulphur,	-	-	.1900 —
104	——— (109)	-	-	.1890 Ir. <i>jr.</i>
105	Ashes of cinders,	-	-	.1855 C.
106	White glass, specific gravity 2.386, (102)	-	-	.1870 W.
107	White clay burnt,	-	-	.1850 G.
108	Black lead,	-	-	.1830 —
109	Sulphur, (103, 104)	-	-	.1830 K.
110	Oxide of antimony, nearly free of air,	-	-	.1666 C.
111	Rust of iron, ditto. ditto,	-	-	.1666 —
112	Ashes of elm-wood,	-	-	.1402 —
113	Iron, (116, 118, 119, 1 ⁵ .3)	-	-	.1450 Ir.
114	Oxide of zinc, nearly freed from air,	-	-	.1569 C.
115	White cast iron,	-	-	.1350 G.
116	Iron,	-	-	.1300 D.
117	White oxide of arsenic,	-	-	.1260 G.
118	Iron, (113, 116, 119, 123)	-	-	.1269 C.
119	Iron, specific gravity 7876,	-	-	.1260 W.
120	Cast-iron abounding in plumbago,	-	-	.1240 G.
121	Hardened steel,	-	-	.1230 —
122	Steel softened by fire,	-	-	.1200 —
123	Soft bar iron, specific gravity 7.724, (118)	-	-	.1190 G.
124	Brass, specific gravity 8356, (126)	-	-	.1160 W.
125	Copper, specific gravity 8.785, (127)	-	-	.1140 W.
126	Brass, (124)	-	-	.1123 C.
127	Copper, (125, 134)	-	-	.1111 —
128	Sheet iron,	-	-	.1099 L.
129	Zinc, specific gravity 7154, (136)	-	-	.1020 W.
130	———	-	-	.1000 D.
131	Nickel,	-	-	.1000 D.
132	White oxide of tin, nearly free of air,	-	-	.0990 C.
133	Cast pure copper, heated between charcoal, and cooled slowly, specific gravity 7907,	-	-	.0990 G.
134	Hammered copper, specific gravity 9150,	-	-	.0970 G.
135	Oxide of tin, (132)	-	-	.0960 K.
136	Zinc, (129)	-	-	.0945 C.
137	Ashes of charcoal,	-	-	.0909 —
138	Sublimed arsenic.	-	-	.0840 G.
139	Silver, specific gravity 10.001,	-	-	.0820 W.
140	Tin, (145)	-	-	.0704 C.
141	Yellow oxide of lead,	-	-	.0680 —
142	White lead,	-	-	.0670 G.
143	Antimony,	-	-	.0645 C.
144	——— specific gravity 6107,	-	-	.0630 W.
145	Tin, specific gravity 7380, (140)	-	-	.0600 W.
146	Red oxide of lead,	-	-	.0590 G.
147	Gold, specific gravity 1904,	-	-	.0500 W.
148	Vitrified oxide of lead,	-	-	.0490 G.
149	Bismuth, specific gravity 9861,	-	-	.0450 W.
150	Lead, specific gravity 115,	-	-	.0420 W.
151	———	-	-	.0352 C.

TABLE OF CAPACITIES.—NO. II.

Liquids.

152	Solution of ammonia, specific gravity 948, (36)	-	1.0500 D
153	Milk, specific gravity 1.026, (12)	-	.9800 —
154	Solution of carbonate of ammonia, specific gravity 1.055, (7)	.9500 D.	
155	Common vinegar, specific gravity 1.02, (54)	-	.9200 —
156	Solution of common salt, specific gravity 1.197,	-	.7800 —
157	Solution of sugar, specific gravity 1.17,	-	.7700 —
158	Alkohol, specific gravity 85, (9, 15, 44,)	-	.7600 —
159	Nitric acid, specific gravity 1.2, (21, 59)	-	.7600 —
160	Solution of carbonate of potash, specific gravity 1.50,		.7500 —
161	Alkohol, specific gravity 817,	-	.7000 —
162	Nitric acid, specific gravity 1.30, (39)	-	.6800 —
163	Acetic acid, specific gravity 1.056,	-	.6600 —
164	Sulphuric ether, specific gravity 76,	-	.6600 —
165	Alkohol, (9, 15, 158, 161)	-	.6400 Les.
166	Nitric acid, specific gravity 1.56, (45)	-	.6300 D.
167	Nitric acid,	-	.6200 Les.
168	Solution of nitrate of lime, specific gravity 1.4,	-	.6200 D.
169	Muriatic acid, specific gravity 1.153, (37)	-	.6000 —
170	Sulphuric acid and water equal bulks,	-	.5200 —
171	Spermaceti oil, (47, 53)	-	.5200 —
172	Olive oil, (35)	-	.5000 Les.
173	Sulphuric acid, specific gravity 1.844,	-	.5600 D.
174	Sulphuric acid, (31, 51, 56)	-	.5400 Les.
175	Quicksilver, (59, 60)	-	.0400 D.

TABLE OF THE CAPACITIES OF GASES FOR CALORIC.—NO. III.

I. REFERRED TO WATER AS A STANDARD.

176	Water,	-	1.0000
177	Air, (3)	-	0.2669
178	Hydrogen gas, (1)	-	5.2936
179	Carbonic acid, (5)	-	0.2210
180	Oxygen, (2)	-	0.2361
181	Nitrogen (6)	-	0.2754
182	Nitrous oxide,	-	0.2369
183	Olefiant gas,	-	0.4207
184	Carbonic oxide,	-	0.2884
185	Aqueous vapour, (4)	-	0.8470

II. REFERRED TO AIR AS A STANDARD.

Specific heats of

				Equal volumes.	Equal weights.
186	Air,	-	-	1.0000	1.0000
187	Hydrogen,	-	-	0.9055	12.401
188	Carbonic acid,	-	-	1.2585	0.8280
189	Oxygen,	-	-	0.9765	0.8848
190	Nitrogen,	-	-	1.0000	1.0518
191	Nitrous oxide,	-	-	1.5505	0.8878
192	Olefiant gas,	-	-	1.5550	1.5765
193	Carbonic oxide,	-	-	1.0340	1.0805

TABLE OF THE SCALE OF TEMPERATURE, AND OF THE EFFECTS PRODUCED AT
DIFFERENT DEGREES, ON A NUMBER OF BODIES.

	Wedg.	Fahren.
Extremity of the scale of Wedgwood,	240°	52277°
Greatest heat of an air furnace 8 inches in diameter, which did not soften Nankeen porcelain,	160	21877
Chinese porcelain softened best sort,	156	21357
Cast-iron thoroughly melted,	150	20577
Hessian crucible melted,	150	20577
Bristol porcelain not melted,	135	18627
Cast-iron begins to melt,	130	17977
Greatest heat of a common smith's forge,	125	17327
Plate glass furnace (strongest heat,)	124	17197
Bow porcelain vitrifies,	121	16807
Chinese porcelain softened, inferior sort,	120	16677
Flint glass furnace (strongest heat,)	114	15897
Derby porcelain vitrifies,	112	15657
Stoneware baked in	102	14337
Welding heat of iron, greatest,	95	13427
Welding heat of iron, least,	90	12777
Cream coloured ware baked in	86	12257
Flint glass furnace, (weak heat,)	70	10177
Working heat of plate glass,	57	8487
Delft ware baked in	41	6407
Fine gold melts,	32	5237
Settling heat of flint glass,	29	4847
Fine silver melts,	28	4717
Swedish copper melts,	27	4587
Brass melts,	21	3807
Heat, by which enamel colours are burnt on,	6	1857
Red-heat fully visible in day-light,	0	1077
Iron red hot in the twilight	-	884
Heat of a common fire (Irvine,)	-	790
Iron bright red in the dark,	-	752
Zinc melts,	-	700
Quicksilver boils (Irvine,)	-	672
----- (Dalton,)	-	660
----- (Crichton,)	-	655
Linseed oil boils,	-	600
Lead melts (Guyton, Irvine,)	-	594
Sulphuric acid boils (Dalton,)	-	590
The surface of polished steel acquires a deep blue colour,	-	580
Oil of turpentine boils	-	560
Sulphur burns,	-	---
Phosphorus boils,	-	554
Bismuth melts (Irvine,)	-	476
The surface of polished steel acquires a pale straw colour,	-	460
Tin melts (Crichton, Irvine,)	-	442
A compound of equal parts of tin and bismuth melts,	-	283
Nitric acid boils,	-	242

	Fahren.
Sulphur melts,	226
A saturated solution of salt boils,	218
Water boils (the barometer being at 30 inches); also a compound of	
5 of bismuth, 5 of tin, and 2 of lead melts,	212
A compound of 3 of tin, 5 of lead, and 8 of bismuth, melts,	210
Alkohol boils,	174
Bees wax melts,	142
Spermaceti melts,	133
Phosphorus melts,	100
Ether boils,	98
Medium temperature of the globe,	50
Ice melts,	32
Milk freezes,	30
Vinegar freezes at about	28
Strong wine freezes at about	20
A mixture of 1 part of alkohol and 5 parts of water freezes,	7
A mixture of alkohol and water in equal quantities freezes,	—7
A mixture of 2 parts of alkohol and 1 of water freezes,	—11
Melting point of quicksilver (Cavendish),	—39
Liquid ammonia crystallizes (Vauquelin),	—42
Nitric acid, spec. gr. about 1.42, freezes (Cavendish),	—45
Sulphuric ether congeals (Vauquelin),	—47
Natural temperature observed at Hudson's Bay,	—50
Ammoniacal gas condenses into a liquid (Guyton),	—54
Nitrous acid freezes (Vauquelin),	—56
Cold produced from diluted sulphuric acid and snow, the materials being at the temperature of —57,	—78½
Greatest artificial cold yet measured (Walker),	—91

The higher temperatures in the above table referred to the pyrometric scale of Wedgwood, are those established on his authority. The observations of Guyton, proving that the degrees of Fahrenheit, assigned by Wedgwood as coinciding with them, are stated too high, have been given in the text, (p. 228.) Guyton has added a table in conformity to his own observations. These again, as referred to Fahrenheit's scale, are certainly too low, as has been stated likewise in the text, and as is evident from the boiling point of quicksilver being stated at 2 of Wedgwood, whereas, from the very construction of his pyrometer, all temperatures indicated by it are necessarily above a red heat. I add this table, however, as, on a subject imperfectly determined, it is of advantage to have comparative results.

TABLE OF TEMPERATURES, BY CUYTON.

	Degrees of Wedgewood.	Degrees of Fahrenheit.
Mercury melts		—39°
Water freezes		+32
Water boils		212
Bismuth melts		475.99
Tin melts		512.48
Lead melts		611.98
Mercury boils	2°	642.75
Zinc melts	3	705.26
Antimony melts	7	955.23
Silver melts	22	1822.67
Copper melts	27	2205.15
Gold melts	32	2517.63
Welding point of iron	95	6508.88
Cast-iron melts	150	8696.24
Porcelain melts	155	9635.68
Manganese melts	160	10517.12
Malleable iron melts	175	11454.56
Nickel melts	175 + x	11454.56 + x
Platinum melts	175 + x	11454.56 + x

TABLE OF FREEZING MIXTURES.

This table gives the powers of different mixtures in reducing temperature, as ascertained by Walker and Lowitz. The experiments of other chemists give results which differ so little from these, that to insert them would be to extend the table without any advantage. The proportions of the substances are not given by Lowitz, but from the context, (*Annales de Chimie*, t. xxii, p. 300), they appear to have been in general equal parts.

	Temperature reduced.	
Muriate of ammonia, 5 parts, nitrate of potash 5, water 16,	from 50° to	10° W.
Muriate of ammonia, 5 parts, nitrate of potash 5, } sulphate of soda 8, water 16,	50 to	4 W.
Nitrate of ammonia 1, water 1,	50 to	4 W.
Sulphate of soda 8, muriatic acid 5,	50 to	0 W.
Sulphate of soda 5, sulphuric acid diluted with an } equal weight of water, 4 parts.	50 to	5 W.
Sulphate of soda 3, nitric acid diluted with an equal } weight of water 2,	50 to	—3 W.
Nitrate of ammonia 1, carbonate of soda 1, water 1,	50 to	—7 W.
Sulphate of soda 6, muriate of ammonia 4, nitrate } of potash 2, diluted nitric acid as above '4,	50 to	—10 W.
Phosphate of soda 9, diluted nitric acid 4,	50 to	—12 W.
2 L		

		Temperature reduced.	
Sulphate of soda 6, nitrate of ammonia 5, diluted nitric acid 4.	}	from 50	to —14 W.
Phosphate of soda 9, nitrate of ammonia 6, diluted nitric acid 4,		50	to —21 W.
Muriate of soda 1, snow 2 parts,		32	to —5 W.
Carbonate of ammonia dry. snow,		32	to —6 L.
Nitric acid diluted. snow,		32	to —10 L.
Concentrated sulphuric acid, snow,		32	to —10½ L.
Muriate of soda 2, muriate of ammonia 1, snow 5,		32	to —12 W.
Soda crystallized. snow,		32	to —15 L.
Potash deprived of its water of crystallization, (la- pis causticus), snow,	}	32	to —15 L.
Concentrated acetic acid, snow,		32	to —17 L.
Carbonate of potash. snow,		32	to —17 L.
Nitrate of lime. snow,		32	to —17 L.
Oxymuriate of antimony, snow,		32	to —17 L.
Muriate of soda 10, nitrate of potash 5, snow 24,		32	to —18 W.
Muriate of magnesia, snow,		32	to —22 L.
Sulphuric acid diluted with one half its weight of water, 2 parts, snow 3 parts,	}	32	to —25 W.
Muriate of soda 5, nitrate of ammonia 5, snow 12,		32	to —25 W.
Acetate of potash, snow,		32	to —26 L.
Muriate of iron, snow.		32	to —27½ L.
Concentrated muriatic acid 5, snow 8,		32	to —27 W.
Muriatic acid and snow,		32	to —30 L.
Concentrated nitrous acid 4, snow 7,		32	to —30 W.
Nitrous acid and snow,		32	to —22 L.
Concentrated solution of potash, snow,		32	to —30 L.
Muriate of lime 3, snow 4,		32	to —40 W.
————— 3, ——— 2,		32	to —50 W.
————— 5, ——— 3,		32	to —53 L.
Potash 4, snow 3,	}	32	to —51 W.
Muriate of lime 2, snow 1,		32	to —53½ L.
————— 3 ——— 1,		0	to —66 W.
Sulphuric acid diluted with half its weight of water 10, snow 8,	}	—40	to —73 W.
		—68	to —91 W.

CHAP. II.

OF LIGHT.

LIGHT, like Caloric, is an agent too subtle to admit of its combinations being accurately traced. It seems to exist in some bodies as a constituent principle, since it is disengaged from them when they enter into new combinations; but we are unable to obtain, in a separate state, the bases with which it is combined. In its chemical history, therefore, we can state only the effects it produces, the circumstances connected with its absorption and evolution, and the results of the researches that have been made with regard to its nature and constitution. Though a material principle, it may be considered as a power producing repulsion. Its particles are repellent, and from its chemical effects it is not improbable that it acts on bodies in part at least by its repulsive force.

The materiality of this agent is sufficiently proved. Its motion, though inconceivably rapid, is progressive, and may be measured; it may be stopt in its progress, or its direction may be changed; it may be condensed into a smaller or dispersed over a larger space; it is inflected when passing near to any body, which proves it to be subject to gravitation; and it produces chemical changes in many bodies, exists in them in a state of combination, and is disengaged by the exertion of new affinities.

Two opinions have been maintained with regard to the nature of Light, both admitting its materiality. Descartes

and Huyghens supposed that the phenomena it presents arise from vibrations propagated through an extremely rare and elastic fluid, which is diffused through all space, and in which fluid luminous bodies have the power of exciting these vibratory motions, as sonorous bodies have the power of exciting vibrations in the air,—an hypothesis which Euler supported. Newton regarded light as an emanation of particles of extreme minuteness, projected in right lines from the sun, and from luminous bodies, and moving with extreme velocity. This opinion has been generally received. It accords better than the other with the phenomena of optics, and appears to be established by the chemical agencies which light exerts, its fixation in bodies, and its subsequent evolution.

If it be received, it is obvious that the minuteness of the particles of light must be astonishingly great, and the imagination requires even some aid to be able to form any conception of it. No better illustration of it can be given than that by Melville. “There is no physical point,” says he, “in the visible horizon, which does not send rays to every other point; no star in the heavens which does not send light to every other star. The whole horizon is filled with a sphere of rays from every point in it, and the whole visible universe with a sphere of rays from every star. In short, for any thing we know, there are rays of light joining every two physical points in the universe, and that in contrary directions, except where opaque bodies intervene.” How great, then, must be the subtlety of these particles, to prevent their interrupting each other; and at what an immense distance must each particle in a ray be placed!

The minuteness of the particles of light may also be estimated by the velocity with which they move. From astronomical observations, it appears that light moves at the rate of nearly 200,000 miles in a second; a particle of light projected from the sun arriving at the earth in about

$8\frac{1}{4}$ minutes. Were not its particles inconceivably small, their momentum, arising from such velocity of motion, must be such as to destroy every substance on which they impinge. Yet it is doubtful whether the momentum they do possess is capable of being ascertained by the most delicate mechanical contrivance. From an experiment of this kind, it has been calculated that the quantity of matter in the rays of light collected by a concave mirror, of two feet in diameter, would not amount to more than one twelve hundred millionth part of a grain; and how many particles of light must be in these accumulated rays!

The particles of light, like those of caloric, appear to repel each other. So perfect is its elasticity, that it is reflected from a body at an angle equal to the angle of its incidence. It is subject to that attraction which is exerted between masses of matter, as, when passing near to a body, it is inflected towards it; and in passing obliquely from one medium into another, it is turned from the direct course in which it was proceeding: If it pass from a more rare into a denser medium, it is bent towards the perpendicular; if from a denser to a rarer medium, the reverse; the degree in which this takes place being different, according to the density and the nature of the medium. This is named the Refraction of light. In some substances the transmitted ray divides into two parts, which proceed in different directions, and thus exhibit a double image: This constitutes Double Refraction. In transmitting one of the divided rays through another double refracting substance in a similar position with the first, each divided ray passes through without any change; but if the second refracting substance, such as a rhomboid of calcareous spar, be turned round while the first is fixed, a separation of each of the divided rays begins to take place: when the eighth part of a revolution is completed each is again divided into two, so that four images of an object can be seen; and when the fourth part of a revolution

is completed, the direction of the rays is changed, and the four are again reduced to two. The change thus impressed on light is named its Polarization. And it has been discovered by Malus, that this property, which had been considered as an effect only of double refraction, may be acquired, by reflection at a particular angle, from all transparent bodies; and even light reflected from opaque bodies is polarized.

A ray of light is not homogeneous, but consists of various rays, which being differently refrangible, are separated when the entire ray is made to fall on a refracting medium at a great angle of incidence. By thus passing a ray of white light through a triangular glass prism, it is divided into seven rays, distinguished by the power of exciting the sensations of different colours, red, orange, yellow, green, blue, indigo and violet. Of these the red is the least refrangible, and therefore falls on a space least distant from that which the entire ray of light would have fallen on, had it passed through the prism without having its direction changed. The violet is the most refrangible; it therefore is at the greatest distance; these two bounding the space which the rays occupy, or the prismatic spectrum as it is termed, the others being arranged in the order above stated, and occupying unequal spaces in the spectrum. They are not perfectly defined, but each passes insensibly into the contiguous one. By transmitting each of these rays through a prism, it is refracted, but without suffering any farther change.

It has often been supposed, that of the seven coloured rays into which a beam of light is resolved by refraction, some are primary, and by their intermixture constitute the others. The unchangeableness of each of these rays by a second refraction, it is justly remarked by Prieur, is not inconsistent with this opinion; for if any coloured ray be formed of other two rays, these must be of the same refrangibility, since it is only from this coincidence that

they could be in the same place of the prismatic spectrum to form the compound ray, and a second refraction cannot be supposed capable of separating them. The red, yellow and blue have been considered as primary rays, as by the intermixture of these colours the others are produced; red with yellow giving orange; yellow with blue forming green; and blue with red, indigo. Priur advanced the hypothesis, that the red, green and violet are the primary rays; the red and green form, when the red predominates, orange; when the green predominates, yellow; the green and violet form blue; and the violet and red, purple. This he considered as established by finding, that on submitting one of the compound rays to transmission through a medium capable of intercepting one of the primary rays, of which it is supposed to consist, the result corresponded with the hypothesis in a variety of trials; and also, by obtaining white light by combining the red, green, and blue rays*.

The coloured rays differ in other properties. Herschel has shewn that their illuminating powers are unequal. By causing the different coloured rays to fall successively on an object under the microscope, he found that the red-making rays are far from having it in any eminent degree; the orange possess more of it than the red; and the yellow rays illuminate objects still more. The maximum of illumination lies in the brightest yellow or palest green. The green is nearly equally bright with the yellow; but from the full deep green, the illuminating power decreases; that of the blue is nearly the same with that of the red; the indigo has much less than the blue; and the violet is very deficient†." These rays exert also different chemical agencies.

The differences in the coloured rays were supposed by

* Nicholson's Journal, vol. xvii, p. 18.

† Philosophical Transactions for 1800, p. 267.

Newton to depend on the different magnitudes of their particles, those of the red ray being supposed to be largest. By others they have been ascribed to the different velocities with which they are projected from the luminous body; the red moving with the greatest, the violet with the least. With whatever probability these hypotheses may explain optical phenomena, they scarcely afford an explanation of the fact, that these rays differ not only in their mechanical properties, and in the sensations of vision which they excite, but likewise in their chemical powers.

* The rays of light have different relations to different bodies. Through some they pass with scarcely any interruption: these are transparent, and, according to Newton, consist of particles of equal density and arranged with uniformity, so that the ray of light meets with no obstacle, and is not attracted from its course. By some bodies the greater part of the rays is reflected. Some reflect one ray retaining the others, which gives rise to the different colours bodies exhibit; and, lastly, there are some by which the light is absorbed, and by numerous reflections and refractions in their pores, is lost, constituting blackness.

Light can also form a more intimate union with bodies. Of this there appear to be different degrees. In many cases it is absorbed without producing any change in the qualities of the body, and is again slowly given out; in others it occasions alterations of temperature and of composition, or acts as an important chemical power.

What is called Phosphorescence seems to depend on the first of these species of union. There are substances which, on being exposed to the solar rays, appear luminous when removed to a dark place, and continue to emit light, for some time; the luminous appearance becomes gradually fainter in all of them, and at length ceases, but it is renewed by exposing them again to the light of the sun. The bodies possessing this property are termed Phosphori, or Solar Phosphori, to distinguish them from

an inflammable substance, Phosphorus, of a quite different nature. This property was first observed in a fossil named the Bolognian Stone (a natural sulphate of barytes.) Margraaf, Du Fay, and others, discovered that many other substances possessed the same quality; and Beccaria and Wilson found that almost every kind of matter in a solid state, the metals and a few other bodies excepted, might be made to emit light, by being exposed to the solar rays.

There is a great difference among these bodies in the quantity of light which they emit. The shells of marine animals, the bones of land animals, some of the gems, marbles, limestone, sulphate of barytes, fluor spar, and other combinations of earths with acids, are the most powerful natural phosphori;—sugar, white paper, and linen, possess the same quality in an eminent degree. In general white bodies are more phosphorescent than those of a dark colour, though to this there are exceptions, and some perfectly white scarcely shine. Many phosphori shine so feebly that the illumination is not observed, unless the sensibility of the eye to light is increased by previously remaining for some time in a dark place, and surveying them when newly withdrawn from the solar light.

Artificial solar phosphori may be prepared, which emit more light, and for a longer time than the greater number of natural phosphori. Of this kind is the Bolognian phosphorus, the substance first discovered to possess this property. The Bolognian stone is a sulphate of barytes, and any variety of this fossil that is pure answers the purpose. It is made red hot in a crucible, and is reduced to a fine powder in a stone or glass mortar (a metallic one being absolutely unfit.) This powder is made into a paste with mucilage of tragacanth, and this is divided into thin cakes, which are to be dried with a gentle heat, gradually increased. A furnace is then to be filled with pieces of charcoal to three-fourths of its height, and the fire kindled. Upon

this are laid the flat cakes, and more charcoal is placed over them so as to fill the furnace. The fire is to be continued till all the fuel is consumed; the cakes are then to be cleansed from the ashes by blowing on them with bellows. They are to be kept excluded from the air.

Another artificial solar phosphorus is that termed Baldwin's. It is nitrate of lime which has been exposed to a red heat in an earthen vessel. Its phosphorescence is inferior to that of the former.

The most powerful of the artificial solar phosphori is that named Canton's. To prepare it, oyster-shells, freed from their impurities by washing, are exposed to a red heat in a common fire for half an hour; the purest part is separated and pounded in a stone mortar: three parts of this powder are mixed with one of sulphur; this mixture is pressed into a crucible, which is placed in a fire, and kept red hot for one hour at least. When it is cold the mass is broken, and the whitest parts scraped off for use*. Or what is recommended in preference to this by Dr Higgins, the oyster-shells, after being calcined without being reduced to powder, are to be put into the crucible in alternate layers with sulphur, and exposed to the requisite heat. This phosphorus, after it has been exposed for a few seconds to the clear light of day, appears luminous in a dark place; and the figures on the dial-plate of a watch may be distinguished by its light.

The light these bodies emit is usually white, but in some of them yellow or red. The phosphorescent property belongs to them in very different degrees. Some require to be exposed to the solar rays to render them luminous, and even to the rays concentrated by a lens. With regard to others, it is sufficient to expose them to clear day-light; after this exposure they are equally luminous as when they have been exposed to the light of the sun, and they con-

* Philosophical Transactions, vol. lviii, p. 337.

tinue longer so, as in the latter case the heat which they receive contributes to expel the light more rapidly. Some can be illuminated by the light of a candle, or by that of an Argand's lamp concentrated by a mirror. The light of the moon, or that emitted from other phosphori is insufficient. The exposure of a few seconds to the light is sufficient to illuminate them, and when exposed for a longer time they are not rendered more luminous. Canton's phosphorus is rendered highly luminous by passing over it an electrical discharge; and Mr Skrimshire has shewn, that a number of saline and earthy substances are illuminated by the same operation, so as to emit light for several minutes after the discharge has been communicated*.

The temperature has a material influence on the phosphorescent property. It is extinguished by the cold of a freezing mixture, but returns as the temperature rises. If heat is communicated, the luminous appearance is increased. Beccaria filled a glass tube with pounded Bolognian phosphorus, and after exposing it to the light, plunged one half of it in warm water, and observed that it gave light more copiously than the part which was in the open air. When a piece of these phosphori has ceased to emit light, it may be rendered luminous by heating it; but when the luminous appearance is thus promoted by heat, it ceases sooner. Mr Canton filled two glass-balls with his phosphorus; illuminated them at the same time, and to the same degree: both were brought into a dark room, and one was put into a bason of boiling water; it shone much brighter than the other, but in ten minutes became quite dark, whereas the other continued visible for two hours after, and even then the heat of the hand rendered it more luminous. When by exposure to a certain degree of heat the phosphorescent body has ceased to be luminous, it

* Nicholson's Journal. vol. xvi, p. 101, vol. xvii, p. 12, vol. xix, p. 153.

may be made to give out light by exposing it to a still higher temperature. By a temperature somewhat below ignition, Canton's phosphorus, which had been kept in darkness more than six months, gave a considerable light.

These facts, and the general phenomena of phosphorescence, lead to the conclusion that the phosphorescent body absorbs a portion of the light to which it is exposed; that this light is again gradually emitted; and that its expulsion is accelerated by heat.

There is, however, an objection to this theory. Du Fay found, that on exposing solar phosphori to light transmitted through coloured glasses, the light afterwards emitted had not the least tint of the colour of the glass *. These experiments were repeated by Mr Wilson: he could not discover any difference in the kind of light emitted by the phosphorescent body, from such an arrangement; and Beccaria, who had at first obtained a different result, also found this to be the case. Even in the more unexceptionable mode of conducting the experiment, of separating the different rays by the prism, and throwing a single ray upon the phosphorescent body, it still emits the light which it does upon merely exposing it to the light of day. If a piece, which in the dark gives a white light, have a red light thrown upon it, it still continues to give out an uniform white light: or if a piece which naturally exhibits the prismatic colours, as some phosphori do, be exposed to a white light, or to any particular ray, its prismatic appearance still remains the same †. Nay, when a specimen is selected which shines with a particular colour, red for example, if the red ray be thrown upon it, it shines, according to Wilson, feebly, while exposed to a different ray, as the violet, it gives its usual red light brilliantly; with the blue, the same, but not so vividly; and with the

* Mémoires de l'Acad. des Sciences, 1735, p. 493.

† Wilson's Experiments on Phosphori.

green less. And, if a piece were selected, which shone with a blue light, it was feebly excited by the blue ray, but strongly by the red *. Seebeck has more lately found, that under exposure to any coloured ray a phosphorescent body still shines with the usual kind of light which it gives out when exposed to white light. These facts are unfavourable to the conclusion, that the light of phosphorescent bodies is that which they had absorbed, and have led to the inference that they shine by their own light, and that exposure to light is only necessary to cause it to be thrown off. It is not improbable, however, that the different varieties of light are convertible into each other, and on this supposition the fact may be accounted for, in conformity with the common theory of phosphorescence.

The phosphorescent property is independent of any action of the air, any of these bodies being equally luminous in a glass vessel hermetically sealed. The phosphorescence is even impaired by long exposure to the air, apparently from absorption of moisture. When the phosphorescent matter is included in a glass vessel, hermetically sealed, Mr Canton found, that the property remains unimpaired for a long time, (four years,) the luminous appearance being produced as at first by exposure to light; but if a little water be included with it, it is soon lost. Alcohol impaired it little, and ether not at all †.

There is another class of phosphorescent bodies quite different from the former, which give out light when heated, independent of any previous exposure to light; this is much diminished at each time the light is emitted, and is not renewed by exposure to the sun's rays. The mode of shewing this phosphorescence, is to throw the body, reduced to powder, on a plate of iron, heated nearly to redness, or to drop it into a hot fluid. In some the light is

* Journ. Physiq. t. xv, p. 93.

† Philosophical Transactions, vol. lviii, p. 339, 342.

momentary; in others it lasts for several minutes: it is in general uncoloured, though, from various bodies, it is also of various colours. Fluor spar is the most powerful phosphorescent body of this family; it emits a beautiful purple, or sometimes a green light; and the variety of it named Chlorophane, not only becomes highly luminous from a very gentle heat, but also shines brightly after exposure to light. Next to fluor spar are different marbles, feldspar, quartz, gems, and other earthy fossils. The luminous appearance is independent of the action of the air, and is of the same intensity in the exhausted receiver of an air-pump, or in different gases. Even liquids give the same light when poured on a hot iron, particularly those of an oily nature, as Brugnatelli has observed.

Attrition also excites phosphorescence in some bodies. It has been long known, that some of the gems when rubbed shine brightly. Two pieces of quartz rubbed against each other become luminous on the surface. And in some fossils, as the tremolite, the phosphorescent property is so great, that friction from a feather excites it.

Mr Wedgwood, by whom a number of experiments was made on the phosphorescence from heat and from attrition *, found, that if the attrition is strong, the light emitted is greater. By applying a piece of agate to the circumference of a wheel of grit, on causing it to revolve, the agate where it touches the stone becomes red hot; if the wheel revolve at a quicker rate, the touching point emits a pure white light and glowing sparks; rock crystal, glass, and other bodies, are in the same way rendered equally luminous. In general, colourless and transparent bodies, whose surfaces become rough by rubbing, give most light. The light is from some bodies colourless, and from others coloured of various shades. It is equally bright in the different kinds of air, and even under water. Mr Wedg-

* Philosophical Transactions for 1792.

wood shewed also that it is not electrical, as on rubbing two pieces of quartz together, and applying them to the fine down of a feather, the down is not sensibly affected: He supposes, that attrition excites phosphorescence by the heat it occasions; this heat is momentary, and confined to the rubbed surface, but it may be sufficiently high to produce the phosphorescent appearance. Bournon has observed, however, that there are fossils which are rendered phosphorescent only by friction, as quartz or corundum; others only by heat, as carbonate of strontites, or of barytes, while there are many which become phosphorescent from either cause, as phosphate, fluate, and carbonate of lime*. The very slight friction, also, which is sufficient to render some bodies luminous, is unfavourable to the opinion of the evolution of the light being owing to the heat which attrition excites.

A light, analogous to phosphorescence, is produced in some bodies by chemical action. It is observed when magnesia, or lime, or pure potash, is thrown into the mineral acids, as well as in the rapid slaking of quicklime by affusion of water†. Dizé has shewn, that it is accompanied with elevation of temperature‡.

There remains to be noticed one other kind of phosphorescence, that exhibited by animal matter, either in a living or dead state. Marine animals are remarkable for this property; almost every kind of marine fish, after having been removed a short time from the water, being luminous in the dark, and some shining with great brightness for three or four days. The flesh of some quadrupeds has been observed to emit light; and a similar light is afforded by certain vegetable substances, as decayed wood, or peat-earth. This species of phosphorescence has been the sub-

* Nicholson's Journal, vol. ii, p. 290.

† Mémoires de Chimie de Pelletier, t. i, p. 35.

‡ Journal de Physique, t. xlix, p. 177.

ject of experiment by Boyle *, afterwards by Canton †, and more recently by Dr Hulme ‡, and Mr Macartney §.

This light does not appear, unless in a few instances, until the animal has been for some time deprived of life; it is always apparent, however, before there are any signs of putrefaction. A certain degree of putrefaction does not seem incompatible with it, as appears from the experiments of Canton; but, according to Hulme, "as soon as a great degree of putrescence has taken place, the luminous property is destroyed, and the light extinguished." He has also remarked, that in the instances recorded of the flesh of land animals being phosphorescent, it appears to have been in a fresh state.

The luminous matter of these substances may be separated, and preserved for a time by certain processes. Canton observed, that sea-water, or a solution of salt of a certain strength, became luminous, from the substance of a fresh herring being immersed in it. Dr Hulme found, that other saline solutions acted as solvents of this luminous matter. About four drachms of the substance of a fresh herring were put into a solution of two drachms of sulphate of magnesia in two ounces of cold water. The liquor the second evening, exhibited a lucid ring placed at the top, and on shaking the phial the whole became beautifully luminous. It continued to possess this property for some time, the luminous matter separating, and being again mixed by agitation; it gradually, however, became less luminous, and on the fourth night was extinguished.

Many other saline solutions, such as those of sea-salt, of nitre, sulphate of soda, &c. have the same property of extracting the luminous matter from marine animals. It is probably from sea-water having dissolved this matter that

* Boyle's Works, vol. iii, p. 157.

† Philosophical Transactions, vol. lix, p. 446.

‡ Ibid. for 1800.

§ Ibid. for 1810.

the ocean appears occasionally luminous, though this appearance seems also to depend on other causes, especially on the presence of phosphorescent animalcula *: and according to Mr Macartney, it is always produced by living animals, and most frequently by the presence of the medusa scintillans. Fresh-water is incapable of extracting this luminous matter, and even prevents the fish immersed in it from becoming luminous. A number of substances extinguish this light, such as pure water, the acids and alkalies, fermented liquors, and ardent spirits; and, what is singular, it is extinguished by saturated solutions of the salts that preserve it when in dilute solutions. Dr Hulme found, however, that in these concentrated solutions the light exists, and may be made to appear by dilution with water, and it may thus be repeatedly extinguished and revived, by adding either salt or water.

The luminous appearance is augmented by motion or agitation; it is impaired, and even extinguished by cold, but is revived, and rendered brighter by a moderate heat. By a great degree of heat, such as that of boiling water, it is extinguished, and does not revive on cooling. It appears to be in some measure dependent on exposure to air, as Dr Hulme found that the parts of fish which were not thus exposed were dark, while the parts exposed were luminous. He did not find it to be brighter in oxygen gas than in atmospheric air. Nitrogen gas appeared to prevent the animal matter from becoming luminous, but did not extinguish it when it had previously begun to shine; hydrogen gas, nitrous gas, carbonic acid gas, and sulphuretted hydrogen gas, not only prevent the luminous appearance, but extinguish it if it had come on. It is also impaired, and at length extinguished in the vacuum of an air-pump, but re-appears when the air is admitted †.

* Letter by Professor Mitchell, Phil. Mag. vol. x, p. 20.

† Philosophical Transactions for 1800.

The emission of light in any of these cases is not accompanied with any sensible heat, the temperature of the luminous matter being the same with that of the surrounding air.

The light from decayed wood appears to be similar. Boyle observed that a piece of rotten wood that was luminous, ceased to shine when placed in an exhausted receiver, and became luminous when the air was admitted *. This has been confirmed by Dr Hulme. It has also been ascertained by Spallanzani, Carradori, Humboldt, and by Hulme and Bockman, that, in nitrogen, hydrogen, carbonic acid, carburetted and sulphuretted hydrogen gases, its luminous appearance is soon extinguished, but is revived when atmospheric air is admitted. Dr Hulme ascertained, too, that luminous wood had the property of shining only when it had been exposed to the air, (or perhaps to the light,) as when newly broken the internal surface did not begin to shine for some time. These facts appear to prove that the emission of the light depends on some action of the air, or of its oxygen. There are others, however, inconsistent with that supposition. Boyle relates, that a piece of rotten wood inclosed in a glass tube which was hermetically sealed, continued to shine as before †. Forster mentions, that luminous wood does not change its appearance when introduced into oxygen, which is confirmed by Hulme and Bockman. And the last experimenter ascertained, that when the luminous appearance had ceased in these gases, a fresh piece of wood shone for some time ‡; and likewise, that the wood when luminous continued to shine for a number of hours in spring water, or in boiled or distilled water, as well as in several saline solutions, and in linseed oil ||. The luminous appearance was extinguished instantaneously by the acids, and speedily by alkohol, as also by a high temperature; though by a moderate heat, as that of 100°, it is rendered

* Boyle's Works. vol. iii, p. 159.

† Phil. Mag. vol. xvi, p. 22.

‡ Ibid p. 180.

|| Ibid. vol. xvi, p. 147.

more vivid, while by cold it is repressed. In all these circumstances, this phosphorescence is similar to that of animal matter.

Certain insects, both alive and dead, emit light occasionally. The glow-worm (*lampyris splendidula*) has been long known from this property ; the light is variable, being at one moment brilliant, and at another weak or extinct. It proceeds from two rings at the inferior part of the abdomen, the phosphorescent matter being included in a receptacle from which it may be expressed. Other insects have a similar property, as the lantern-fly of the West Indies. Mr Macartney has enumerated a number of these phosphorescent animals, all of them belonging to the classes of insects, worms, mollusca and zoophytes : the phosphorescent matter from a number of them is liquid, but appears in all to observe nearly the same laws. It continues to shine for some hours, and is rendered brighter by friction and by warmth, but it cannot be inflamed. Experiments on this kind of phosphorescence have been made, however, principally on the glow-worm. Forster observed, that in oxygen gas it shines with more splendour than in atmospheric air, and the brilliancy is also more permanent, but it fades when removed from the oxygen. The gas did not appear to be impaired in its purity. Forster conceived the luminous matter to be a secretion from the animal, connected with its respiration, and shining more when the air is inspired than when it is expired ; whence he explains its variable light *. According to Carradori †, the luminous appearance depends on the will of the animal. The phosphorescent matter obtained from its receptacle by compression, shines in oil or in water, as well as in the air, and likewise in the Torricellian vacuum ; and the animal itself shines when immersed in water, and

* Journal de Physique, tom. xxiii, p. 24.

† Annales de Chimie, tom. xxvi, p. 96.

with more splendour in tepid than in cold water. The luminous appearance being brighter in oxygen gas, Caradiori supposed, owing to the stimulus which the gas communicates to the animal. The fact itself, however, is doubtful, as Dr Hulme did not find that the glow-worm, either dead or alive, shone with more splendour in oxygen gas than it does in atmospheric air. Mr Macartney found, that some of the luminous medusæ shone not only under water, but likewise under ardent spirit, and in an exhausted receiver. Dr Hulme states, that this species of phosphorescence agrees with the others in being extinguished by hydrogen, carbonic acid, sulphuretted hydrogen, and nitrous gases, and in returning when the animal is removed to the atmospheric air. The evolution of light in the living animal appears to be accompanied, according to Mr Macartney's observations, with a production of heat; but this does not take place after death, though the light continues to be emitted.

The next general fact to be noticed in the chemical history of light, is its power of producing heat. This property is sufficiently obvious. The action of the solar rays is the great source of the heat of our globe, and, when concentrated by a mirror or lens, affords nearly the most intense heat we can command.

Different substances are unequally heated by the rays of light; transparent bodies allowing them to pass through with little interruption, are comparatively little heated. White coloured substances are less heated than those which are of a dark shade. Franklin, by laying pieces of cloth of different colours on snow, while the sun shone upon it, found that the darker coloured cloths were most heated, as was rendered evident by their sinking deepest in the snow. A thermometer blackened and exposed to light rises higher than a thermometer, the bulb of which is clean.

In giving the history of Radiant Caloric, I have stated the fact in general, that the different rays of light have different heating powers. Dr Hutton had formed a conclusion of this kind, probably from some imperfect observation or experiment. "The compound light," says he, "which is white, has a greater power of giving vision, in proportion to its power of exciting heat; whereas, in the red species it is the opposite; for here the power of exciting heat is greater, in proportion to its power of giving vision *." Rochon had before investigated the subject more completely, though his experiments had attracted little notice. He found, that an air thermometer exposed to the action of the different coloured rays, separated by a prism, rose from the violet to the red; and the proportion of heat between clear red, and the most intense violet, appeared to be nearly that of 8 to 1: the heat of the yellow orange differed little from that of the red, so that the hottest rays seem to be between the clear red and the yellow; and from these the heat diminished considerably more towards the violet than towards the red. The experiments at the same time were attended with several discordant results, and were confessedly imperfect †.

More lately this was made the subject of experiment by Herschel, whose attention was directed to it, by finding, in employing different coloured glasses in viewing the sun, that from some of them he felt a sensation of heat, though with little light, while others gave light with scarcely any sensation of heat. He employed the following apparatus. In a piece of pasteboard, mounted on a frame so as to be moveable, an opening was cut, a little larger than the ball of a thermometer, and of a sufficient length to let the whole extent of one of the prismatic colours pass through. A prism being placed at right angles to the so-

* Dissertation on Light and Heat, p. 38.

† Philosophical Magazine, vol. xiv, p. 408, 413.

lar ray, and turned until its refracted coloured spectrum became stationary, the moveable frame with the pasteboard was adjusted so as to be perpendicular to the rays coming from the prism; and beneath were delicate mercurial thermometers, which could be more or less advanced, so that one only of the prismatic rays should fall on the bulb. The heating powers of the different rays were thus ascertained. It was found that they increase progressively from the violet to the red, and in the following proportions: The thermometer rose in the red ray, in ten minutes, 7° of Fahrenheit; in the green ray, the rise in the same time amounted only to $3\frac{1}{2}^{\circ}$; and in the violet ray, in the same time likewise, to two degrees*.

Herschel, in the prosecution of his experiments, farther obtained the important result, that the heating power extends beyond the visible spectrum on the side of the red ray. When the opening in the pasteboard was made to coincide with this space, the thermometer rose half an inch beyond the red ray, the heat was even greater than in the red ray, and within this was the maximum of effect; it could be traced farther however: at the distance of an inch the rise amounted in thirteen minutes to $5\frac{1}{4}$ degrees; and the heating power was discernible to the extent even of $1\frac{1}{2}$ inch†. On the other side of the spectrum beyond the violet ray no heat was found.

Since the calorific rays occupy a larger space than the visible rays, they must be of more extensive refrangibility; and hence, when the solar rays are concentrated by a lens, the focus of heat must be different from that of light. On making the experiment, Herschel found reason to conclude, that it is farther from the lens than that of light, probably not less than one-fourth of an inch‡.

These experiments were repeated and confirmed by Sir

* Philosophical Transactions for 1800, p. 258—9.

† Ibid. p. 286—7.

‡ Ibid. p. 444.

H. C. Englefield, a differently arranged apparatus, so as to guard against reflected heat, being used. A prism was placed in the proper position, in an open window; the coloured spectrum from it was thrown on a lens of 4 inches in diameter, and about 22 inches focal length. The lens, as well as its mounting, was covered with a thick white pasteboard skreen, in which was cut a slit of 3 inches long, and half an inch wide over the centre of the lens, and through which any of the prismatic colours could be transmitted, while the others were excluded. A sensible mercurial thermometer, with a naked bulb, was placed so that the bulb was in the focus of the lens, and the coloured rays were successively thrown on the bulb. The rise was as follows:

In the blue, in	-	3'	from 55° to 56°
— — green, in	-	3'	from 54 to 58
— — yellow, in	-	3'	from 56 to 62
— — full red, in	-	2½'	from 56 to 72
— — confines of the red,		2½'	from 58 to 73½
Quite out of visible light,		2½'	from 61 to 79

These denote the greatest effect of the different rays. When the bulb of the thermometer was blackened, the rise was greater, being in the full red ray in 3' from 65° to 82°; in another experiment, to 87°, and in the invisible ray to 98° *. It was beyond the full red light, and where a very faint blush of red was perceptible, that the greatest heat was discovered; and even half an inch beyond the edge of the red ray, and where there was no illumination whatever in the focus, the heat was still greater than in the red ray itself, the rise in the former being in 3' from 69° to 79½°; in the latter, in 3', from 67° to 71½°.

Mr Leslie inferred from some experiments, that the difference in the heating power of the different coloured

* Journals of the Royal Institution, vol. i, p. 203.

rays, is even greater than that stated by Roehon or Herschel, the amount being between the two extremes of the violet and red, as 1 to 16; and the proportions between the blue, green, yellow, and red rays being nearly as 1, 4, 9, 16. He denies the existence of any heating power beyond the red rays.

Berard, subsequent to these researches, submitted the subject to experiment, and with peculiar advantage; as from the nature of his apparatus he was able to obtain a ray of light perfectly stable, and thus to avoid the principal fallacy, that from the instability of effect in comparing the different rays. His experiments confirm the general result, that the heating power increases progressively through the coloured rays of the spectrum, from the violet to the red: he did not find, however, the maximum of effect to be beyond the red ray, as Herschel and Englefield had found, but to be within the spectrum, and exactly at the point where the bulb of the thermometer was entirely covered with the red light; but he also found, that the heat could be traced sensibly beyond the red ray, though it became progressively less as the distance increased; and at the place beyond the visible spectrum, where Herschel had fixed the maximum, it amounted only to one-fifth of what it was in the red ray. The absolute intensity of heat produced was also less than in Herschel's experiments. These differences might in part arise, as Berthollet suggests, from the nature of the prism, and the difference of the apparatus. The caloric rays, Berard ascertained, were liable to the same laws as the luminous rays, in transmission through a medium producing double refraction; as in passing a beam of solar light through a rhomb of calcareous spar, the caloric property was found to be gradually less from the violet to the red, and also to be traced beyond the visible rays; and hence the caloric power, whether it belongs to the luminous rays or not, is

divided along with them in passing through the spar. He also found, that the calorific rays undergo polarization, and the same result was obtained on those discharged from a body highly heated *.

All these experiments appear to prove, that the solar beam consists not only of rays of visible light, but likewise of rays of radiant caloric. If this be established, it follows as a probable conclusion, that the heating power of the solar rays may not depend on the rays of visible light, but on the rays of radiant caloric associated with them. The rays of heat, like those of light, may be of unequal refrangibility. If so, they will be separated by the prism, and spread over a certain space : this space may coincide with that occupied by the rays of visible light ; the one spectrum will be blended with the other, and the visible rays of light will to common observation appear to possess certain degrees of heating power, though, apart from the rays of caloric, they possess none ;—a conclusion which becomes still more probable from the fact, that the heat is less considerable in the prismatic spectrum, as the distance is receded from where the calorific rays are accumulated.

To determine if this conclusion were well founded, Dr Herschel made an extensive series of experiments. Assuming that the illuminating property is characteristic of light, he inferred, that if the heating power be a property belonging to the visible ray as such, and not owing to any calorific ray associated with it, both properties ought, when the ray is transmitted through any transparent medium, to be equally diminished. We are not to expect that it will pass through with its powers undiminished. But it may be expected, that if the heating and illuminating power depend on the same matter, whatever portion of this matter be retained, these powers must be dimi-

* *Annals of Philosophy*, vol. ii, p, 161.

nished in the same proportion ; while, if the heating and illuminating powers do not depend on the same matter, but the one on rays of caloric, and the other on rays of light,—it may happen that these will be unequally acted on by the medium through which they are transmitted ; one may be retained in larger quantity than the other, and hence the heating and illuminating powers will be unequally diminished. On submitting this to trial, Herschel found, from an extensive series of experiments, on transmission of light through different kinds of glass, different coloured glasses, and different fluids, that they are not proportionally diminished, but that in some cases the illuminating is more diminished than the heating power, and in others the reverse happens. He found, for example, that of 1000 incident rays, “a yellow glass stops only 333 rays of heat, but stops 819 of light : on the contrary, a pale blue stops 812 rays of heat, and but 684 of light. Again, a dark-blue glass stops only 362 rays of heat, but intercepts 801 of light ; and a dark red glass stops no more than 606 rays of heat, and yet intercepts nearly all the light, scarcely one ray out of 5000 being able to make its way through it*.

These experiments being made on undecomposed light, a comparison can be less easily instituted from them, as to the effect of transmission on the heating and illuminating powers of any single prismatic ray ; and it may even be said, that they prove only the difference, in transmission, between the calorific rays and the luminous rays in general ; not that the heating power of the coloured rays is owing to the presence of rays of caloric. It is more conclusive, to have the experiment confined to a single prismatic ray ; to separate it from the others, transmit it through a certain medium, and observe the effect produced on its illuminating and heating powers. If the ray

* Philosophical Transactions for 1800.

be homogeneous, there will be a diminution in both in the same proportion ; while, if it be heterogeneous, or consists of rays of light and heat, these will probably be unequally stopped, and the heating and illuminating powers must be unequally diminished.

To take one example : “ Is the heat which has the refrangibility of the red rays occasioned by the light of these rays? Should that be the case, as there will then be only one set of rays one fate only can attend them, in being either transmitted or stopped, according to the power of the glass applied to them.” With regard to the fact on this point, Dr Herschel states, that from a series of experiments, he finds, that red glass does not stop red rays of light ; “ but with regard to the rays of heat, the case is just the reverse ; the red glass stops not less than 692 out of a thousand, of such rays as are of the refrangibility of red light.” He adds, “ Here, then, we have a direct and simple proof, in the case of the red glass, that the rays of light are transmitted, while those of heat are stopped, and that thus they have nothing in common but a certain equal degree of refrangibility, which, by the power of the glass, must occasion them to be thrown together into the place which is pointed out to us by the visibility of the rays of light *.” This conclusion admitting the fact seems just. Did the heating power apparent in the red ray, (and of the prismatic rays, it is the one which possesses it in the greatest degree,) depend on the visible light of that ray, and belong to it as one of its properties ; since this light is not stopped by red glasses, the heat likewise ought not to be stopped. Nearly two-thirds of the heat, however, are arrested, a proof that heat arises, not from the visible light of the ray, but from calorific rays associated with it, which, by such a glass, are transmitted only in this proportion.

* Philosophical Transactions for 1800.

In some of Berard's experiments, it appeared, that when the entire solar beam was transmitted through transparent colourless glass the heat is not separated from the light. But this does not invalidate Herschel's results.

The experiment, too, of separating the light and caloric emitted from burning fuel, affords a proof that the heating power does not depend on visible light. By placing a piece of transparent glass before the fire, the radiant caloric is in a great measure arrested ; the light is transmitted, and may be collected in a focus, in which is little sensible heat.

These discoveries open a new view of the nature of light, and of the constitution of the solar ray. No fact appeared more undoubted than that light has a power of exciting heat ; and when the solar beam was resolved into its different coloured rays, it was supposed that it was analysed, and that these were its sole constituent parts. It appears that both these propositions are false. A solar ray consists of the different visible rays of light ; but with these are associated rays of caloric. These two *kinds* of rays not only differ from each other in refrangibility, but each appears to be composed of rays of unequal refrangibility. Hence, when decomposed by the prism, each is spread over a considerable space. The radiant caloric is less refrangible than the rays of light ; it is therefore found beyond the prismatic spectrum on the side where the less refrangible visible rays are ; but being composed of rays of unequal refrangibility, it is not confined to that space, but is intermingled with the different coloured rays, diminishing as these become more refrangible. To this intermixture the heating power which these coloured rays appear to have in different degrees is to be ascribed ; and apart from this radiant caloric we have no reason to believe that light has any heating power. Of light without heat we have an example in the rays of the moon. De la Hire observed long ago, that when collected in the focus of a

burning mirror 35 inches in diameter, they did not sensibly affect an air thermometer *.

Mr Leslie, assuming that the intensity of light may be estimated by the heat it excites, has employed his differential thermometer, with a particular modification, as a Photometer. One of the balls of the instrument is made of black enamel, the other of clear glass; the rays of light which fall on the latter pass through with little interruption, and little heat is therefore produced; those which fall on the former are absorbed, exciting a higher degree of heat. This continues to accumulate, until any farther increase is prevented by an opposite dispersion of heat from the rise of temperature in the ball; it then remains stationary: the air in this ball being of course more expanded than the air in the opposite ball, the liquid in the tube connected with it descends, and the extent of its descent measured by the scale attached gives the intensity of the light. A glass case is put over it to exclude the effect of any current in the atmosphere around. The instrument is an elegant one, but is deficient, as resting on a principle far from being established, that heat and light are the same, or even that the intensity of light may be judged of by the heat it produces. Heat is not the sole effect produced by light; there are others which accompany it, and these are not proportional to it. The property of illumination itself, that is, the power of affecting, with a certain vividness of impression, the organ of vision, is not proportional to the heating power: for measuring both by the coloured rays, the illuminating power is greatest in the middle of the spectrum, while the heating power increases towards the red extreme; and a species of mingled light may be conceived of in which those effects shall not be proportional. The chemical powers of light too are not connected with the heating power, but are even in oppo-

* Mémoires de l'Acad. des Sciences, 1704.

sition to it, and a light in which the violet ray predominates shall appear by the photometer to be weak, while, judged of by another effect, equally characteristic of light, it shall appear strong.

The last part of the history of Light is that which relates to what may be more peculiarly termed its Chemical power,—its agency in occasioning combination and decomposition. This is in many cases strikingly exemplified; and particularly so in expelling the element oxygen from many of the combinations in which it exists.

Where this element is not retained in combination by a very strong affinity, light alone is able to effect its separation, partially or entirely. In nitric acid, oxygen is in this state, and accordingly, by exposing this acid to the rays of the sun, it acquires a yellow, and at length an orange hue,—a change owing to a partial separation of its oxygen. If therefore the phial be filled with the acid, and closed with a glass stopper, the change, as Mr Kirwan has remarked, does not happen, the separation of the oxygen gas being prevented by this mechanical force; while, if the phial be only half filled, it takes place on exposure to the solar light for a quarter of an hour*; and if the phial containing the acid have a bent tube connected with it, terminating under an inverted jar, in a few days a considerable portion of oxygen gas is collected, as Berthollet ascertained†.

Another acid, the oxymuriatic, suffers a similar decomposition from light. Berthollet exposed it in a flask, with a bent tube, to the light of the sun; in a very short time bubbles of air were disengaged, which were found to be pure oxygen gas. The oxymuriatic acid became colourless, and was converted into muriatic acid‡.

The combination of metals with oxygen is often sub-

* Notes to Scheele's Essay on Air and Fire, p. 230.

† Journal de Physique, tom. xxix, p. 82.

‡ Ibid. p. 81.

verted by light. If the compounds of gold and silver with this element be exposed to the solar rays, their colour becomes darker, and if their compounds with acids be submitted to the same exposure, their colour is even more darkened. A piece of paper moistened with a solution of silver in nitric acid, is blackened in a few minutes: the muriate of silver, the *luna cornea* of the older chemists, is still more susceptible of this change, and is hence the most delicate test of the chemical agency of light. It is partly from this action of light that it alters the shades of metallic paints.

The decomposition of these compounds is even sometimes complete, and the metal is obtained in its original state. Scheele evaporated a solution of gold to dryness, and dissolved the dry mass in distilled water, poured it into a crystal phial shut with a glass-stopper, and exposed it to the beams of the sun. A fortnight after, minute spangles of gold appeared in the solution, and the surface was covered with a fine pellicle of gold *. Mrs Fulhame, in a series of experiments on metallic reduction, established similar facts. A piece of silk, dipt in a solution of gold, was exposed to the sun-beams, and kept moderately wet with water during the experiment; from being yellow, it acquired first a green, then a purple colour; at length particles of gold appeared on its surface, and, “in about an hour, the whole of the silk was covered with a superb coat of reduced gold.” A piece of silk treated in the same way, but put aside in a dark place, suffered no change in three months, except that its colour became brown. A solution of silver was also reduced by the action of light, while in the dark it suffered no change †.

It appears, that in some of these cases, the acid only of the compound is separated, which, however, equally proves

* Essays on Air and Fire, p. 83.

† Essay on Combustion, p. 142, 146, 151.

the chemical agency of light. It had been supposed, that the blackening of the muriate of silver is owing to the disengagement of its oxygen, and the approach of the silver to the metallic state; but Berthollet found it to be owing to the separation of a portion of its acid, which, when the experiment is made under water, remains in that fluid *.

The operation of bleaching affords another example of the chemical changes which light is capable of producing. Colour is in this case removed, and this depends equally on the transfer of oxygen, the colouring matter of the thread receiving that principle probably from the decomposition of the water with which the substance to be bleached must be supplied. This formed the old method of bleaching; and the substitution of the oxymuriatic acid in the new mode, establishes this theory of the changes of which the operation consists.

Even the processes of animated nature are influenced by the chemical agency of light. "Organization, sensation, spontaneous motion, and all the operations of life," says Lavoisier, "exist only at the surface of the earth, and in places exposed to the influence of light; and without it nature itself would be inanimate." Its operation in vegetation is strikingly exemplified in the adaptation of plants to particular climates. Those which grow under a clear sky, and an intense solar light, are in general more pungent, odorous, and aromatic, than those which are placed under the opposite circumstances; and plants which are the natives of a warm climate will not grow or produce their fruit in situations where they are less exposed to its genial influence. The artificial exclusion of light from vegetables giving rise to the process named Etiolation or Blanching, affords another proof of its action in vegetation. The plant always extends its branches towards any opening at which light may enter; and if this be closed,

* Chemical Statics, vol. i, p. 147.

and another opened in a different situation, it changes the direction in which it was shooting, and turns still towards the light ; and in this way, as L'Abbé Tessier has shewn, plants may be made to grow in any direction. If kept in perfect darkness, they become feeble, succulent, insipid, and of a white or yellowish colour, while, if transferred to a situation where they enjoy the solar rays, they regain their green colour, and become vigorous. These changes from the exclusion of light appear to be owing to the accumulation of oxygen in the plant, as under its influence, this principle is disengaged from their leaves, derived probably from the decomposition of water, and perhaps of other compounds subservient to vegetable nutrition. According to the experiments of Tessier and Decandolle, the light emitted by a lamp gives even a green colour to the leaves, though less deep than that from the light of day. The light of the moon has a similar effect *.

Nor are animals exempt from the influence of this important agent. Deprived of it they suffer nearly the same changes as vegetables do, and the darkness of their colour is in general greater according to the intensity of the light to which they are habitually exposed. Insects which live under ground are usually of a light shade : the animals of the arctic regions are almost all pale or white, while those belonging to the tropical countries are distinguished by the variety and brilliancy of their hues. Even in man we trace a gradation of colour proportioned nearly to the climate in which he resides.

Light, it appears from some late observations, not only occasions chemical decomposition, but in some cases promotes combination. Gay-Lussac and Thenard observing its effect in decomposing oxymuriatic acid, and finding that this acid is decomposed in a similar manner by an elevated temperature, drew the conclusion which had often

* Mémoires de l'Acad. des Sciences, 1783, p. 155.

been maintained, that light and caloric are the same in their action on unorganized bodies. The action of light however is slow, and this suggested the idea that it might produce chemical changes in cases where, from this slowness, its influence had not been observed; and in particular they supposed this might happen in the mutual action of two aëriform bodies; for since this action is not exerted at once, it cannot arise entirely from their mutual affinity, but must in part be owing to the action of some external cause, which favours the exertion of that affinity, such as the influence of heat or light. They prepared accordingly some mixtures of this kind, particularly that of oxymuriatic gas and hydrogen gas, two gases which are known to act slowly on each other. When the mixture was placed in darkness, no action appeared to be exerted between them after several days; but when it was exposed to weak solar light, the mutual action was nearly complete in a quarter of an hour. And when the mixture was exposed to the direct solar rays, immediate inflammation, with detonation, was produced. Similar results were obtained with mixtures of oxymuriatic gas, and the different compound hydrogen gases*.

The same fact had been discovered by Mr Dalton. He observed a great variation in the rapidity of action between oxymuriatic acid and hydrogen gases, and he found this to be owing to the action of light, the action being slow when the light was imperfect, more rapid when the light is freely applied, and, under actual exposure to the solar rays, so rapid as to be attended with explosion†.

From the experiments of Chaptal, it appears, that the process of crystallization, especially that form of it in which capillary crystals shoot up the sides of a vessel containing a saline solution, is influenced by light. He found this to

* Mémoires d'Arcueil, tom. ii, p. 347.

† System of Chemical Philosophy, p. 300.

take place only on the side of the vessel which was illuminated; he could thus cause it to rise at any side, and when the vessel was shaded, the line of separation was distinctly marked by the limit of the crystallization. Metallic salts shewed this phenomenon best *.

Scheele proved, that the decompositions produced by light arise from its chemical agency, not from its heating power. He exposed the substances which suffer changes from light, to the rays of the sun, in a phial covered with a thick coating of black paint; and though the phial became very hot, the substances contained in it did not undergo the least change, even after an exposure for several days to the operation of the sun-beams †. Berthollet made a similar experiment; that of exposing oxymuriatic acid to the rays of the sun, in a phial covered with black paper, when it suffered no alteration, nor gave out any air, as it does from the direct exposure to light. Did the light operate by the heat it excites, its effects under such circumstances ought to be the same, or greater, as even more heat was communicated.

Rumford, on the other hand, stated some experiments ‡ to prove, that light has no peculiar chemical powers, further than what depend on the heat it excites. He shewed that a piece of silk wetted with metallic solutions, such as a solution of silver or gold, when exposed to the heat of a wax taper, suffered a partial reduction to the metallic state, similar to that which they suffer from light,—a proof, as he supposed, that the effect from light depends on the heat it excites. He farther found, that when a solution of gold or of silver was put with small pieces of charcoal into a tube, and exposed to a heat of 212° , the gold or silver was reduced on the surface of the charcoal to the me-

* Journal de Physique, t. xxxiii, p. 297.

† Essay on Air and Fire, p. 96.

‡ Philosophical Papers, p. 341.

tallic form. But it is probable, that in both experiments the effect arose from the agency of charcoal present in the first case in the smoke of the flame, and in the second directly applied; and, accordingly, Berthollet, in repeating the latter experiments, found that the aërial products disengaged shewed that it was the charcoal which had operated*. The question is, Can heat *alone*, to the extent in which it is produced by the solar rays, produce the chemical effects which these rays occasion? There is no unequivocal experiment by which this is established.

What is the power of the different prismatic rays in producing these chemical effects? We are indebted to Scheele for the first observation on this interesting question. Having refracted the sun-beam by a prism, he put a piece of paper impregnated with muriate of silver in the coloured light, and it became sooner black in the violet than in any of the other rays†. This experiment was repeated by Senebier, who ascertained the comparative powers of the different rays. The shade produced in the muriate of silver, by exposure to the violet ray for 15 seconds, required for its production the action of the purple ray to be continued 23 seconds, of the blue 29, of the green 37, of the yellow $5\frac{1}{2}$ minutes, of the orange 12 minutes, and of the red not less than 20 minutes‡. Phosphorescence too appeared in some experiments by Englefield to be unequally excited by these rays, the blue ray having a greater power in rendering Canton's phosphorus luminous than the others.

These results have been more lately established by Seebeck||. When a mixture of oxymuriatic gas and hydrogen gas was exposed to the solar light under a glass of a red colour, it suffered any change very slowly, while under a blue

* Chemical Statics, vol. i, p. 149.

† Essay on Air and Fire, p. 91.

‡ Mémoire. Physico-Chymiq. t. iii. p. 199.

|| Nicholson's Journal, vol. xxiv, p. 220.

glass decomposition immediately occurred. Solar phosphori exposed under the different prismatic rays were very differently affected. From the violet ray they exhibited the greatest illumination, rather less from the blue, much less from the green, still less from the yellow, and from the red the luminous appearance was lost. When exposed beyond the violet ray, where scarcely any light was visible, the luminous effect was as great as in the violet ray itself. Beyond the red ray it was in some cases excited, but feebly. When the phosphorescent body was exposed to light transmitted through thick blue glass, it shone; but under orange coloured glass it exhibited no luminous appearance, and was even extinguished when previously luminous from exposure to white light*.

The analogy, that as there is thus a decrease in the chemical power from the violet ray, on one side of the spectrum through the others, so there is a decrease in the heat-power, in the contrary direction, from the violet towards the red; and the still more direct analogy of the ex-

* A singular property exerted by the violet ray of light is that of exciting magnetism. The fact seems to have been discovered by Morichini, an Italian philosopher; it was for some time denied, but it appears to be established. The solar ray being decomposed by a prism, and the other rays being intercepted on a screen from the violet, a needle, or thin plate of steel, in which no magnetic polarity can be discovered, is placed horizontally; the violet ray being collected into a focus is carried along the needle proceeding from the centre towards one of the extremities, taking always the same extremity, and taking care, as in the common operation of exciting magnetism, not to go back in the opposite direction. In about an hour the needle becomes strongly magnetic. According to Morichini, and to another experimenter, Ridolfi, who has continued the investigation, the experiment succeeds only under a clear and bright atmosphere; and the presence of clouds, or of humidity in the air, prevents it. *Annals of Philosophy*, vol. ii, p. 390. *Annales de Chimie et Physique*, t. iii, p. 323.

istence of invisible calorific rays in the solar beam, naturally suggested the inquiry, whether invisible chemical rays might not exist beyond the violet ray.

Ritter appears to have made the first experiments on this subject. He placed muriate of silver without the solar spectrum, next to the violet ray, and found it to be blackened. On placing it beyond the red ray, it not only did not suffer this change, but if previously a little blackened, became white; phosphorus was kindled in the one space, that beyond the red ray, and extinguished in the other. The muriate of silver under the action of the violet ray was rather less blackened than in the space beyond it, where the invisible chemical rays existed, and still less in the other visible rays. He concluded, therefore, that there are two species of invisible rays, besides the visible rays in the solar beam, one species calorific, and which promote oxidation, the other capable of separating oxygen when it is combined, and of counteracting its combination *. Dr Wollaston had about the same time made similar experiments, and, by the blackening of muriate of silver, had discovered the existence of invisible rays beyond the violet ray, capable of producing this chemical effect. He did not succeed in restoring the white colour to muriate of silver, after it had been once tinged, however slightly, by exposure to the more refrangible rays. What is singular, guaiacum, which is rendered green by exposure to light, apparently from the absorption of oxygen, suffers, according to Dr Wollaston, this change in the violet rays of the spectrum, and at the other extremity, instead of suffering it, has its yellow colour restored †. Berard confirmed the results of Ritter and Wollaston with regard to the greater degree of chemical energy towards the violet side of the spectrum, and its existence even to a small dis-

* Nicholson's Journal, vol. v, p. 255, & vol. viii, p. 214.

† Ibid. vol. viii, p. 293.

tance beyond that extremity: it decreased rapidly in the blue and indigo rays, and when that portion of the coloured rays which extends in the spectrum from the green to the red was concentrated by a lens, although the illumination was extremely brilliant, the muriate of silver remained exposed to it for more than two hours, without any alteration, while, when exposed to that portion extending from the green to the violet concentrated in a similar manner, although the light was much less vivid, and the heat less strong, it became blackened in less than ten minutes*.

If we might reason by analogy, from the law proved by Herschel to be observed in the refrangibility of the invisible calorific rays, we should conclude that the invisible chemical rays may also be of unequal refrangibilities; that therefore they may not only exist in the space beyond the violet ray, but be spread over the prismatic spectrum, and that the visible rays may owe to them their chemical powers. We shall thus have three species of radiant matter in the solar beam, each distinguished by a single property not possessed by either of the others; the rays of light possessing the power of exciting illumination; the rays of caloric producing heat; and the invisible rays distinguished by their power of occasioning chemical changes. It has been affirmed, that Ritter, by transmitting the coloured rays through different prisms, has separated them from the chemical rays, and produced a coloured spectrum devoid of chemical action†. He is also said to have made the experiment of uniting the two species of invisible rays, by transmitting by two lenses each species of invisible ray, so as to bring the space beyond the violet ray and that beyond the red ray to correspond; but from this intermixture, no illumination was obtained; the power of the chemical rays appeared to predominate.

* Nicholson's Journal, vol. xxxv, p. 256.

† Ibid. vol. viii. p. 216.

Instead of supposing, according to the preceding view, three species of rays in the solar beam essentially different from each other, distinguished by the respective characters of exciting heat, producing illumination, and causing chemical decomposition, it is no doubt possible to represent the subject under a different point of view. Light, it is remarked in a report by Berthollet and Biot on the experiments of Berard, may be composed of rays unequally refrangible, and consequently unequally attracted by bodies, which supposes original differences in their masses, their velocities, or their affinities. These rays may also differ in their power of exciting heat, of affecting the organ of vision, and of causing combination or decomposition. It is more probable to suppose that vision should not be affected except under certain limits of refrangibility, and that an extreme of this quality, either too much or too little of it, should render the rays incapable of producing the effect. In like manner, the calorific quality, and that of chemical power, may vary through the whole extent of the spectrum at the same time as the refrangibility, but according to different functions, so that the calorific quality expressed by one shall be at its minimum at the violet extremity, and at its maximum at the red, while the chemical power being expressed by another shall be at its minimum at the red, and acquire its maximum at the violet, or a little beyond it *.

This is a mode of expressing the facts in a form somewhat more obscure than the simple statement of them, rather than the expression of any theory or induction with regard to them. Herschel had suggested a similar view, in so far as regards the distinction of the visible and invisible rays, but with more precision. The invisible rays may consist, he remarked, of "rays of light that have such a momentum as to be unfit for vision. Admitting as high-

* Nicholson's Journal, vol. xxxv, p. 257.

ly probable that the organs of sight are only adapted to receive impressions from particles of a certain momentum, it explains why the maximum of illumination should be in the middle of the refrangible rays, as those which have greater or less momentum are likely to become equally unfit for impressions of sight."

Any explanation of this kind, however, is liable to very obvious objections. We do not find that either species of invisible ray, that beyond the red, or beyond the violet, is capable, by condensation, of exciting illumination. Neither by combining these two species of invisible rays is any species of coloured light produced, which ought to be the result did the visible rays differ from the two kinds of invisible rays, by having merely an intermediate degree of momentum, or an intermediate degree of any particular power or function whatever. And, lastly, how are the decrease, on the one side, of the chemical power of light while its heating power increases, and, on the other side, the increase of the chemical with the decrease of the heating power, to be explained? An increase of momentum, of attraction, or of any other quality, might increase both, or a diminution of it diminish both; but on no hypothesis that these rays are gradations of the same matter, possessed of heating and of chemical power, can it be explained how the one should be diminished as the other is augmented.

The opinion has often been maintained, that light and caloric are the same, an opinion founded on the intimate connection subsisting between them. Light is a common source of heat: it produces it when in a state of intensity: they are frequently disengaged together, and, when bodies are highly heated, they always become luminous. Light, therefore, has been supposed to be convertible into heat; and *vice versa* caloric has been supposed capable of passing into rapid projectile motion, and in this

state to constitute light. This theory has been long and generally maintained. The opposite opinion, that light and caloric are different, has likewise been supported on the principle, that their properties are essentially different. Caloric is diffused over matter slowly and equally, and penetrates every body, producing expansion, fluidity, and vaporisation, and giving rise to the sensation of heat, but incapable of exciting illumination. Light, instead of merely raising the temperature of bodies, produces chemical changes, which are not produced by the degree of heat it excites, and which do not arise even from the operation of caloric. Nitrous is converted into nitric acid by heat, but nitric acid exposed to light is converted into nitrous. Such differences in properties, and in chemical powers, have been supposed sufficient to authorise the conclusion, that they are different kinds of matter. On these two hypotheses, scarcely capable of precise determination, it will be sufficient to offer a few observations.

If the hypothesis, that light and caloric differ only in their state with regard to motion, were true, it follows, that in every thing except what relates to this they should be identical; that therefore caloric must be capable of producing the same chemical changes as light; and that light must, when absorbed by bodies, produce heat.

The first of these propositions is sufficiently evident. The chemical agency of light cannot be supposed to depend on its mechanical motion, but on the affinities it exerts. In producing the phenomena which arise from these, it enters into combination, loses its projectile motion, and becomes quiescent. Quiescent light is supposed to be nothing but caloric; hence the introduction of caloric into a body should produce the same chemical changes as light, which, as has already been shewn, is not the case.

Rumford endeavoured to explain this, by observing that many of the changes which light produces are produced by heat when the temperature is raised; and the same argu-

ment has been stated by Gay-Lussac. Rumford also observed, that when rays of light strike on a solid body, or on a quantity of fluid, the thermometer affords no information as to the heat which is exerted at the points on which the rays impinge: it gives merely the temperature of the mass, while the points on which they strike may be momentarily heated to an intense degree; hence light may actually operate chemically by the high degree of heat it excites.

This appears at first view not improbable. But, in the first place, there is no proof that these decompositions can in any case be effected without the agency of light; for where they are occasioned by heat, this must always be raised to ignition, when of course light is introduced. And it farther appears to be refuted by the decisive fact, that the rays of light, which are most powerful in producing heat, such as the red, are the least powerful in occasioning these chemical changes; while the rays which produce them with most rapidity, as the blue and violet, are those which have least heating power. It is obvious, that this is incompatible with the supposition, that the chemical changes which light produces are owing, not to the affinities it exerts, but the heat it excites, and that on the latter hypothesis the results ought to be precisely the reverse. The chemical changes produced by light cannot therefore be owing to the heat it excites, but must be ascribed to some other agency in modifying chemical attraction, and so far light is different from caloric.

If light and caloric were the same, differing only in their state with regard to motion, light must, when absorbed by bodies, produce heat. Here the fact appears at first view to be consistent with the theory, nothing being more familiar than the heating of bodies by the solar rays; and it is this coincidence which has given the strongest support to the opinion; but Herschel's discoveries have rendered this doubtful, since they have shewn, that the heating power of the solar rays is owing to the presence of rays not ha-

ving the properties of light ; and that apart from these, the visible rays have no such power. We have, strictly speaking, therefore, no reason to infer, that light excites heat ; and the inadequacy of any hypothesis to establish this connection between them has been illustrated.

The phenomena of phosphorescence are unfavourable to the hypothesis of the identity of light and caloric. By exposing a phosphorescent body to light, a portion appears to be absorbed, and becomes quiescent ; it is not, however, converted into caloric, but remains in the body as light, and is gradually emitted as such. Were light, caloric in projectile motion, the light must have been converted into heat, and could not be emanated in this form.

With regard to the difficulties supposed to be attached to the opinion that Heat and Light are essentially distinct, the principal is that of accounting for the production of heat by the solar rays. This, however, it is obvious, is now to be referred to the action of the calorific rays in the solar beam, and that before any argument can be drawn from this, these must be proved to be of the nature of visible light.

The phenomena of ignition have been supposed favourable to the opinion of the identity of light and caloric, light being expelled merely by the temperature being raised, and this for an indefinite time if the temperature is kept up. The caloric, therefore, is supposed to assume the form of light. The light emitted, however, may be merely that contained in the body, expelled by the repulsive agency of caloric ; and the continuance of its emission affords no argument against this, when we consider the extreme subtilty of light. The quantity of light which can be absorbed by a phosphorescent body, in exposure for a minute to the solar rays, is sufficient to render it luminous for many days. If, therefore, the high temperature weaken the affinity of light to bodies, it is not difficult to conceive that from this subtilty of light, they may

continue luminous while that temperature is kept up. The light in ignition may also be derived from the same source as the caloric is supplied from; for when ignition is excited by the communication of heat, light is always communicated along with it. There is only one case at least in which this does not appear to be the case,—it is that of the experiment by Mr Wedgwood already described, (p. 303.), in which ignition was excited by the communication of air heated but not luminous. This seems to prove that heat is convertible into light: *Caloric* alone appears to be supplied by the air; yet *light* is given out by the body suspended in it. It is accordingly stated by Berthollet as proving the identity of light and caloric*.

This experiment may be easily explained. Illumination is excited only when a certain number of rays come from a body to the eye; and if the number be diminished, though many rays may still be emitted, the illumination is not perceived. We have sufficient proof of this in phosphorescent bodies, which, when in a weak state of phosphorescence, require the sensibility of the eye to be increased by remaining in the dark for some time, to admit of their illumination being perceived, as Beccaria and Wilson have amply shewn. The same is true with regard to ignition itself: an ignited body being visible in the dark, while in day-light it is obscure, owing evidently to the rays it emits being too few to excite the sensation of vision, when the eye is stimulated by rays of light from every object around it. It is therefore easy to conceive, that every particle of an aëriform fluid may be in a state of ignition; yet it shall not, from its minuteness, be visible; and the mass shall not appear luminous, merely from its tenuity. But if a current of air in this state be directed on a solid body, the common law of ignition will be observed; the ignited particles applied to the solid will render it incan-

* Chemical Statics, vol. i, p. 421.

descent, and preserve it so, and that solid, from its density, will appear luminous.

The production of ignition by friction or percussion is an example in which there is not the supply of light from an external source ; but the difficulty as it relates to this is the same with regard to caloric as to light : we can no more conceive the unlimited emission of the one than of the other, and the light evolved is probably that separated by the high temperature which the percussion excites.

The fact of light and heat being often evolved together, has been supposed to prove an intimate connection between them ; caloric, when evolved rapidly, partly assuming the form of light, while when evolved more slowly it appears as heat ; the degree of light, it is said, being “*cæteris paribus*” proportionate to the velocity with which the caloric is emitted,” and there being no illumination “from bodies which, during their combination, emit the caloric either slowly, or in circumstances in which manifest impediments prevent the projection of it with the velocity necessary to the constitution of light.” Where light and caloric are evolved from a combination, the more rapidly it takes place, the quantities will appear greater, because more are extricated in a given time ; but that the rapidity of combination does not determine the evolution of light, or cause caloric to appear under that form, is obvious in many cases of chemical action : in the combination, for example, of nitrous gas and oxygen gas, or muriatic acid gas and ammonia, in which no light is evolved, though there is no obstacle from the density of the product, or any other cause, to prevent the caloric from assuming, if it were capable of it, the projectile state, which is supposed to constitute light. No regular law, in fact, is observed with regard to this : there are examples of heat being evolved without light, heat with small quantities of light, and light with inconsiderable evolutions of caloric, and these in all varieties of rapidity of combination and condensation, and if, when the heat is considerable, there is generally an ex-

trication of light, this is probably owing to a high temperature weakening the affinities of bodies to light.

The consideration which is most in favour of the opinion that Heat and Light are the same, is the gradual and progressive modifications assumed by caloric in its different forms of radiation. The rays discharged from a heated body are evidently of the nature of caloric, since their abstraction causes reduction of temperature; when they are projected at a temperature not very greatly elevated, they have apparently a weak projectile force, since they are scarcely capable of penetrating transparent media; when they are discharged at a higher heat, they acquire this to a greater extent; there is thus a gradation to the calorific rays in the solar beam; and between both, there is a close analogy in the laws of refraction, reflection, and polarization. From these, again, there is a transition to the rays of light, and ultimately to the invisible chemical rays. And the consideration, that all of these are associated, and that when separated by the prism, they still conform to similar laws, is favourable to the supposition that they depend ultimately on the same power. The differences, however, which exist between them, it has already been remarked, cannot be satisfactorily accounted for from any known, or even any probable cause: And the analogies connecting them, though so far apparent, are not altogether strict. In the progression from the solar calorific rays to the luminous rays the transition is abrupt, and this is still greater in the circumstance of the calorific rays not having the chemical powers connected with light. The whole subject must be considered as involved in so much difficulty and uncertainty that no very certain conclusion can be drawn with regard to it, though the important differences between caloric, considered as the cause of temperature, and light in its usual forms, suggest as the more probable opinion that they are essentially distinct, or that some principle or force exists in light different from heat.

CHAP. III.

OF ELECTRICITY AND GALVANISM.

FROM the phenomena denominated Electrical, the existence of a certain agent or subtle principle has been inferred. This principle, Electricity, besides the specific phenomena arising from its action, is productive of chemical effects, and is so far therefore an object of chemical science. Galvanism, there is reason to believe, is ultimately the same principle with that on which electrical phenomena depend; but as the modes of exciting them, and the effects they produce, are different, I have placed their history under different sections. The operation of this principle, whether under the form of electricity or galvanism, cannot be ascribed to affinities which it exerts as a material substance, if even its materiality be admitted, but must be referred to its action as a general force communicating repulsion, or modifying attraction. It is therefore properly classed with Light and Caloric, and with these it has besides very intimate relations, being capable, under peculiar arrangements, of producing the utmost intensity both of heat and illumination.

SECT. I.—Of *Electricity*.

If a glass rod be rubbed with a piece of dry silk, in a short time light will dart from its surface; and on presenting to it small pieces of straw, or other bodies easily moved, they will first be attracted, and then repelled. The phenomena thus produced are those classed as Electrical, and the glass rod is said to be electrically excited. All bodies, however, are not susceptible of being brought into this state. If the experiment be repeated with a metallic rod, no sensible effect is produced. Hence the distinction of bodies in their relation to electricity into two classes; Electrics, or those which afford it, from friction, and Non-electrics, or those which are incapable of being excited, or of presenting, from that cause, electrical phenomena.

If, when an electric is under excitation, a non-electric be brought near to it, the electricity excited in the former is carried off by the latter. But if an electric be applied in the same manner to the one which has been excited, it will not carry off the excited power. Hence another distinction is established, of Conductors and Non-conductors; the latter being the same as electrics, or those in which electricity is excited by friction, the former the same as non-electrics, which are incapable of this excitation. Glass, resinous substances, sulphur, oils, and aëriiform fluids, are the principal electrics or non-conductors; the principal conductors or non-electrics are metals, saline and earthy substances, and water. But, by certain arrangements, some belonging to the one class may be made to receive the property which is characteristic of the other.

If an electric, when subjected to friction, be insulated, that is, supported on a non-conductor, the quantity of e-

lectricity evolved is inconsiderable, and is soon limited. But, if a communication of it with the earth be established by a conductor, it will afford electricity as long as the friction is kept up; and a conductor insulated, if placed before it, will receive the electrical power, and retain it until another conductor is applied to it. On this being applied, the accumulated electricity is instantly carried off, and in this way a stream of electricity can be obtained. It may also be procured in a more concentrated state, by abstracting it less rapidly. On these principles, the common electrical machine is constructed. It consists of a glass plate or cylinder, which is made to revolve against a cushion, supported on a glass pillar, but connected with the earth by a metallic chain: a large metallic tube, named the prime conductor, is placed before the plate or cylinder, and insulated by being supported on a pillar of glass: the electricity excited by the friction of the plate or cylinder against the cushion is collected by the prime conductor, and on the approach of any conducting substance passes off under the form of a stream or spark.

Electricity, then, is excited by the friction of an electric; but electric excitation is presented under two different modifications, which constitute a distinction of great importance, that of Vitreous and Resinous, or Positive and Negative Electricity.

If a glass rod be excited by friction with woollen cloth, on approaching to it a light body, as a small bit of cork, the cork is first attracted, in a short time it is repelled, and is not again attracted until it has been touched by a conducting body. But if a rod of sealing wax be excited by friction with the cloth, the cork, in the state in which it is repelled by the glass, is attracted by the wax, and on the other hand is repelled by the wax when in that state in which it is attracted by the glass. These electrics present also the electrical light under different forms. If a pointed conductor, as a needle, be presented to the glass,

a round lucid point appears on its extremity in the dark ; but if presented to the wax, a pencil of rays seems to issue from the needle. And if two bodies in these different states be brought into contact, they attract each other, at the same time the electricity in the one appears to neutralise that in the other, and the electrical phenomena soon cease. These two electricities being first obtained, the one from glass, the other from resinous bodies, by friction, were named the Vitreous and the Resinous, and were regarded as essentially different.

It was discovered, however, that when two electrics are rubbed against each other, the one acquires always the one electricity, the other the other. Thus, in the common electrical machine, when the cushion is insulated, on friction being made, it exhibits what has been named the resinous, while the glass gives the vitreous electricity, so that if a cork ball be suspended in connection with the one, and a similar ball be suspended at a short distance in connection with the other, or with the prime conductor in communication with it, they attract each other. And, by certain management, particularly employing different substances to excite friction, or by altering the surface, the same electric may be made to exhibit either electricity, glass the resinous, and sulphur or sealing-wax the vitreous.

Franklin, from these facts, was led to deny that these electricities were different, and to explain the phenomena on a more simple hypothesis,—that there exists only one agent by which they are produced,—a fluid highly elastic, or repulsive of its own particles, but attracting and attracted by the particles of other matter ; that in all bodies a portion of this principle is present, and when present in them, in the proportion natural to each, they exhibit no electrical phenomena ; but, if subjected to certain operations, particularly to friction, the equilibrium is disturbed, and the body either acquires more, or has less, than its

natural proportion. In the former case it is said to be electrified *plus*, in which state it presents the phenomena ascribed to what was called the vitreous electricity: in the latter case it is said to be electrified *minus*, which corresponds with the state of resinous electricity; and hence instead of these terms, the phrases Positive and Negative electricity are employed in the Franklinian theory. This theory, or rather hypothesis, accorded with the phenomena of electricity: it explained very well the excitation of the different electrical states, where the one body always passes into the one state, the other into the other; as in the common electrical machine, where the silk cushion, yielding part of its electricity to the glass, becomes negative, while the latter becomes positive. It has never been established, however, by any rigorous evidence, nor has the opposite hypothesis been disproved, or even shewn to be inconsistent with facts. Assuming the existence of two fluids, each of which repels its own particles, but attracts those of the other, which are contained in all bodies, but are separated by certain causes, particularly by friction, which when separate give rise to what are termed the Positive and Negative electric states, and which when united produce that equilibrium which is not discoverable by any electrical phenomena,—admitting these assumptions, the phenomena of electricity can be explained. The experiments, which have been supposed to shew the direction of the motion of the electric fluid, and by which of course the positive and negative states of a body with regard to it, it is imagined, are discovered, are admitted to be fallacious or inconclusive, and are solved on the hypothesis of two fluids, by the supposition that the facility with which the one is conducted, is somewhat different from that of the other. The principal advantage of Franklin's system is its superior simplicity. On the other hand, the phenomena of galvanism prove, that the two electricities, whatever may be the relation between them, exert diffe-

rent chemical agencies; and hence, whatever theory be adopted, it has become more necessary, in their chemical history, to distinguish between them.

When the prime conductor of the electrical apparatus is excited, on approaching to it within a short distance, a conductor, such as a metallic ball, a luminous train or spark darts from the one to the other, and a similar appearance is exhibited in the transfer of electricity from one body to another at a sensible distance in any elastic fluid. This spark is capable of exciting heat, as well as of conveying electrical effects.

When a glass bottle or jar is coated externally and internally with tinfoil to within three or four inches of its top, and a metallic rod passes into the cover adapted to its aperture, so that the rod or a chain attached to it touches the side or bottom of the jar within, (an arrangement named the Leyden Bottle or Jar,) on applying the rod to the prime conductor of the electrical machine positively excited, the positive state of electricity is communicated to the internal surface of the bottle, and at the same time the external surface, if it is in communication with the earth by means of a conductor, passes into the negative state. If in this charged state of the two surfaces, a conductor, such as a metallic arc, be applied between them, the equilibrium is instantly restored; and a body placed in the circuit is powerfully acted on by the discharge, strong sensations or muscular contractions for example, are excited, and heat in higher intensity than that from the spark is produced. A number of such jars may be so connected by communicating wires, that the internal surface of the whole shall be in one state, and the external surface in the other; and from the discharge of such a battery, by a communication being formed between the two surfaces, effects proportionally more powerful are obtained.

There is another mode in which the electrical state is

induced,—that by induction or position. If a conductor insulated, a metallic rod, for example, supported on glass, be placed opposite to an excited electric, and at a short distance from it in the atmosphere, the extremity of the rod opposite to the excited electric passes into the state of electricity, the reverse of that in the latter, and the other end of the rod passes into the other state, while in the middle the natural state exists; and a series of conductors may be thus excited. The production of the spark and the charge of the coated jar appear to depend on this principle of induction.

Electricity is excited by other causes than by friction. Certain bodies by mere contact, even when every precaution is taken to avoid friction, alter the state of electric equilibrium, one becoming positive, the other negative; at least they are found to be in these states after their separation; and such a relation exists between the assumption of these states, and the chemical constitution or nature of bodies, that some are disposed to become positive, others negative; that body, for example, which has the most powerful attraction to the element oxygen, passing to the former state, that which has a weaker attraction to oxygen passing to the latter. The application of heat, too, in some cases, excites the different electrical states: certain crystallized fossils, more particularly, exhibit this result, such as the tourmalin, the boracite, and others; the crystal at one extremity, or on certain planes becoming positive, and in the extremity or on the planes opposed to these becoming negative. In fusion and in congelation, the experiments of Wilcke and Æpinus have shewn, the different electricities are excited, the states of *plus* and *minus* being produced in the body which has suffered the change of form, and the matter with which it has been in contact during the change: the same thing happens in the formation and condensation of vapour. And there is rea-

son to believe, that similar changes are the consequences of chemical action.

The chemical agencies of electricity are connected with its attractive and repulsive forces ; with its power of exciting heat ; and probably in part with its relation to light.

The attractive and repulsive energies of electricity are dependent on its different states ; and with regard to these, the following laws exist, important, more particularly, in relation to the chemical changes which arise from voltaic electricity. *First*, Bodies in the same state of electricity, whether positive or negative, repel each other : the body A being positive, will repel the body B also positive ; or, if both are negative, they will equally repel. *Secondly*, Bodies in different states of electricity attract each other ; the body A being positive, and B being negative, they display a mutual attraction which causes their approximation and contact. *Thirdly*, A body in the natural state is attracted by a body either positively or negatively electrical. *Lastly*, Two bodies in the different electrical states, when brought into contact, neutralize each other ; the electric excitement in each ceases, and their mutual attraction therefore ceases to operate. These attractions and repulsions are exerted at sensible, and if the electrical excitation be high at very considerable distances. Their application to the chemical changes which arise from the operation of voltaic electricity falls to be considered under its history.

Heat is produced in the production of the electric equilibrium, from the different electrical states ; and the utmost intensity of it can be obtained, and apparently for an unlimited time, when the two forces, the positive and negative, are supplied as the equilibrium proceeds, as is well displayed in the contact of two conductors from the extremities of a voltaic battery. And in the transmission of the electric force, the transmitting medium under a cer-

tain degree of electrical intensity conveyed through it, sustains elevation of temperature. It is not easy to assign the theory of this connection of heat with electricity. The unlimited evolution of heat, in particular, in the neutralization of the two electricities, presents a difficulty which in our present imperfect knowledge of the nature and relations of these powers cannot be satisfactorily solved.

In the transmission of electricity through a conducting body, the degree of heat produced is, in some measure, proportional to the resistance opposed to the quantity transmitted; and hence, when there is no sensible resistance, there is no sensible heat. Van Marum placed the bulb of a very sensible thermometer in a cavity in a brass plate, five inches in diameter, and eleven in length, which was suspended by silk strings near the conductor of his powerful electrical machine. Neither from positive nor negative electricity was there any rise of temperature, nor was any perceived when the bulb was placed in a cavity in a piece of charcoal. But if it was suspended loose between two conductors, so as to have the stream of electricity directed upon it, it rose 80 or 100 degrees of Fahrenheit's scale*. When a thermometer is placed between imperfect conductors, its temperature is raised. Nairne observed, that when the bulb was placed in the luminous current between two balls of wood, it rises 32 degrees; and Van Marum found, that in placing it in a cavity in a rod of wood, placed between the ball of the conductor and the conducting rod of his apparatus, it rose in five minutes from 61° to 112° . In its concentrated state, under the form of the spark, it is capable of kindling inflammable bodies, as ether, or spirit of wine; or if transmitted through mixed gases, having mutual affinities, it acts on the mixture as a spark from an ignited body would, and

* Philosophical Magazine, vol. viii, p. 193.

causes them to combine. This power is still more conspicuous in the discharge from a coated jar, or from an electrical battery ; a heat is produced sufficient, according to the strength and celerity of the discharge, to ignite, and even to melt the most refractory of the metals. From the highest charge of a battery, containing 135 square feet of coated surface, Van Marum found he could fuse 180 inches of iron wire, $\frac{1}{150}$ th of an inch in diameter, or 6 inches of iron wire $\frac{1}{40}$ th of an inch ; from a charge of a battery of 350 square feet of coated surface, 25 inches of the latter wire were melted ; and, from the discharge of a battery of 550 square feet of coating, an iron-wire, $\frac{1}{40}$ th inch in diameter, and 24 inches long, was thrown to a distance in small red-hot globules. A discharge on quartz, one of the most infusible minerals, rounded its corners and points, and even fused a part of it.

From the heat produced by electricity being thus dependent in part on the resistance opposed to its transmission, arises the circumstance, that a quantity which, if passed through a metallic wire of moderate thickness, will produce little heat, on being transmitted through a similar wire, of only one-tenth the diameter of the other, will extricate a quantity sufficient to melt it. Hence, too, if a quantity of electricity be discharged on a metallic wire, sufficient to melt it, on discharging on the same wire a quantity a little less, the rise of temperature is not merely a little inferior to what was excited in the first experiment, but is inconsiderable. From this fact, Berthollet revives an opinion once maintained, of what was termed a Cold Fusion being produced by electricity ; or, as he states it, the electricity operates in fusing bodies, not “ by elevation of temperature, but by a dilatation which separates the particles of bodies.” The hypothesis is a vague one ; and in reference to this very question, it has been proved, that when a body loses its solidity from an electric dis-

charge, it is actually fused, and with elevation of temperature*.

Van Marum found the order of fusibility in the different metals by the electric fluid to be different from that by the direct application of heat. The same quantity of electricity being discharged through wires of the same diameter of the different metals, 120 inches of zinc were melted; the same of lead; of iron 5 inches; of gold $3\frac{1}{2}$; and of silver and copper not quite a quarter of an inch. Hence, it appears, that lead and zinc are equally fusible by the electric fluid, though different degrees of heat are necessary to melt them; and iron, though much less fusible than gold or silver by heat, is melted in greater quantity by the electric fluid. It is possible that different metals differ in the resistance they oppose to the transmission of electricity, and perhaps also the heat excited by that agent may be similar to that produced by friction or percussion, of course connected with the vibratory motion of the bodies subjected to it, and therefore in part dependent on their capability of being put into such a state.

From its power of exciting heat, electricity favours chemical combination, and in particular cases is a more convenient form of applying heat for that purpose than any other. Its power in promoting combination is exemplified in the change it produces on the surface of metals through which it is transmitted, while they are exposed to the atmospheric air. It causes them to combine with the oxygen of the air; and if the electric discharge has been powerful, the change is effected through the whole substance of the metal. It is principally, however, to promote the combination of gaseous bodies that electricity is applied; and it has the peculiar advantage that it allows us to apply heat, and at the same time not admit the air. The apparatus employed is a thick glass tube, Fig. 50,

* Priestley's History of Electricity, 4to, p. 317—18.

closed at one end, perforated with small holes, at about $1\frac{1}{2}$ inch from the end, in which are fixed by cement two metallic wires, the extremities of which, within the tube, are distant one-eighth inch. Any mixed gas intended to be acted on being introduced into the tube previously filled with water or quicksilver, so as to depress the fluid a short space below the wires, the electric spark is transmitted through the mixture, from the extremity of the one wire to the other, by approaching the small ball at the extremity without to the excited conductor of the electrical machine, a chain being hung on the opposite wire. In the mixture of some gases a single spark is sufficient to cause the combination to proceed through the whole mixture. In other cases, a stream of sparks requires to be transmitted to produce the combination to any perceptible extent. Where the combination is attended with explosion, which is the case in firing mixtures of an inflammable gas with oxygen gas or with atmospheric air, the violence of the explosion may sometimes depress the water in the tube to the bottom, and drive out a little of the gas. And if, to prevent this, the mouth of the tube be accurately closed, there is both the risk of the tube being broken in the explosion, and a vacuum is formed after the combination, whence the air which the water holds dissolved escapes and adds to the volume of the residual gas. To obviate these inconveniences, Volta employed a particular apparatus, designed chiefly to be employed as a eudiometer, in determining the quantity of oxygen present in any gas by detonation with hydrogen. Gay-Lussac has lately given a description of one more simple. It consists, Fig. 51, of a thick tube of glass closed at the top by a ring of brass, *ab*, through which passes a wire, terminated without by a ball, and within by another ball, *c*; opposite to this is a similar ball, *d*, to receive the electric spark, supported on a thick metallic wire, *ef*, which is twisted in a spiral form so

as to remain firm by being in contact at different parts with the sides of the tube. To the lower end of the tube a brass ring, *gh*, is adapted, and to this is fixed by a screw, *q*, a circular plate, *ik*, moveable around the screw, which has in the centre a conical opening closed by a valve, which, when in motion, is supported by the stalk, *mn*, this is pressed down by the explosion, and again rises the small pin, *n*, fixing the height to which it can rise. To afford greater firmness to the plate, *ik*, it is inserted within a small notch, *k*, wrought in the projection, *l*, of the ring, *gh*. A ring with a handle is adapted to the middle of the tube, which can be pressed firm by a screw, by which the instrument is held in the hand when the spark is to be taken *. This instrument, I have found, may be rendered considerably more simple with the same advantages, by employing merely a circular piece of caoutchouc as a valve, placing it over an aperture in a brass plate fitted by a screw to a ring on the extremity of the tube, in such a manner that it is pressed down by any expansion from within the tube, and is raised up by pressure from without, so that water surrounding it enters. Or, what affords perhaps a preferable method, a small caoutchouc bottle may be fitted by a screw to a ring on the end of the tube. If the bottle compressed a little be filled with water when the tube containing the gas is adapted to it, room is left for the expansion without any vacuum being formed, while the instrument is also perfectly close.

By the same agency, electricity is able to effect chemical decomposition. If the spark is taken in a compound gas, it separates its constituent parts ; or if an interrupted electrical discharge be sent through water, it is attended with the disengagement of a small quantity of elastic fluid, which consists of the elements of water. Other compound fluids, as alkohol, are decomposed in a similar manner ;

* Annales de Chimie et Physique, tom. iv, p. 189.

and if the metallic oxides be exposed to a strong explosion from a battery, they are reduced to the metallic state*.

Electricity is intimately connected with light. When it passes through the air from one conductor to another, it exhibits a luminous spark; when discharged through the vacuum of an air-pump, it presents vivid corruscations; these appear even, though more faintly, in the Torricellian vacuum. In transmission through any fluid, the fluid, if not in large quantity proportioned to the discharge, is rendered luminous†; or if discharged in large quantities over the surface of a solid, a brilliant illumination is produced. The electrical light is also heterogeneous, or consists of the different refrangible rays. Priestley observed these by a prism; and Morgan has remarked that the electric light assumes different colours according to the medium in which it is taken; sometimes the more refrangible rays being separated, sometimes the less. A spark conveyed through a vacuum not perfect, displays the indigo rays; in the vapour of ether it is green, and in ammoniacal gas red. Or if the electric discharge be transmitted over a piece of insulated wood, by placing the wires between which the discharge takes place at different distances from the wood, the light will exhibit nearly all the prismatic colours‡.

The nature of this relation of Electricity to Light is as imperfectly understood as the nature of its relation to Heat, and the intimate connection subsisting between these three powers forms at present indeed one of the most difficult subjects of chemical theory. The peculiar agencies of electricity in subverting combination apparently unconnected with them, and depending more immediately on the attractive and repulsive forces which it exerts in its differ-

* Philosophical Magazine, vol. viii, p. 197, 319.

† Philosophical Transactions, vol. lxxv, p. 198.

‡ Ibid. vol. lxxv, p. 205.

ent states, involve a subject of investigation not less obscure ; while these agencies, displayed more peculiarly in galvanic arrangements, demonstrate more clearly the great importance of electricity as a chemical power.

SECT. II.—*Of Galvanism, or Voltaic Electricity.*

GALVANISM is apparently the same principle as electricity. Admitting this, however, its effects, and its mode of production, are so far peculiar, that it is proper to consider it under a separate section. Our knowledge of this agent is of recent date. Galvani, an Italian physiologist, observed the first striking phenomenon, which, becoming the subject of investigation, led to the discovery of the principle which has from him derived its name ; though Volta is the philosopher to whom we are indebted for any adequate knowledge of its development and powers, and from whom the name ought to have been derived.

Some observations having occurred to Galvani on the facility with which the muscular fibres of a frog are excited to contraction by electricity, he was led to some experiments, from which the discovery resulted, that by applying a conductor of electricity to the nerve and muscle of an animal, contractions are excited. He inferred from this, that the two parts are in different states of electricity, one *plus*, the other *minus* ; and that the application of the conductor causes the discharge, whence the contraction in the muscle is produced. The subject was prosecuted by other physiologists, and the term Animal Electricity was applied to the agent concerned in this phenomenon, from the hypothesis that it was generated in the animal system,—an hypothesis apparently deduced from these phenomena, and supported by the analogy drawn from the

electrical animals, the Torpedo, *Silurus electricus*, and *Gymnotus electricus*, in whom therē is evidently displayed the power of the living system to produce electricity.

Volta considered these phenomena under a different point of view. It had been found, that by coating the nerve of the animal with metal, the contractions excited are considerably stronger; Volta concluded that the electricity is generated by the metal, not by the animal; and that the introduction of living matter into the arrangement, only renders evident the production of small quantities of this power. His experiments shewed that the connection of a nerve with a muscle is not requisite, but that if two metals be applied to different parts of a muscle, on connecting them by an electrical conductor, contractions are excited. He shewed also that in a similar way *sensations* can be excited; that when one metal, for example, is applied to the under surface of the tongue, and another to the upper surface, on bringing their edges into contact, or connecting them by a conductor, a peculiar taste is felt*.

For some time the prosecution of these experiments, and the discussion of the questions they involved, engaged the attention of philosophers. At length the capital discovery by Volta of a mode of augmenting greatly the galvanic energy, demonstrated the falsity of the hypothesis, that its production is a process of vitality, introduced into science a new principle, and conferred on chemistry an instrument of nearly unlimited power. And this discovery, it deserves to be remarked, was not the result of accident, and scarcely in any degree of the progress of the department of knowledge with which it was connected: it was the fruit of pre-conceived theory, or rather hypothesis, and but for the application of that theory might have for ever remained unknown. In this respect, perhaps, the Pile of Volta stands unrivalled in the history of philosophy.

* Letter of Volta, Philosophical Transactions, 1793, p. 10.

Volta's arrangement consists of two plates of different metals in contact, forming a series, with a liquid interposed between each pair of plates. Upon a plate of metal, suppose of silver or copper, is placed a similar plate of another metal, suppose zinc, and over this a piece of card or cloth of the same size, previously moistened with water, or rather with a saline liquor: this series of copper, zinc, and moistened card, is repeated in the same order, and in this way a pile, consisting of a number of pieces of each metal, is reared, as represented Fig. 64, Pl. VI. Between each pair of plates, electricity is generated; the one metal, the zinc, becoming positive, the other, the copper, negative; the extremities are in the opposite electrical states, so that a wire from either applied to a delicate electrometer causes divergence. If one finger, moistened, be applied to the top of the pile, and another finger, moistened, to the under plate of the pile, the moment this contact is established, a sensation is felt, somewhat similar to an electrical shock, and electrical phenomena can be obtained from the contact of conducting wires with the two extremities.

Another arrangement, similar in principle, which Volta used, is that which he names the *Couronne de Tasses*, represented Fig. 67. It consists of a series of glass cups nearly filled with water, or a saline solution. In the first is put a plate of metal, suppose silver; from this plate there is a wire or thin flat piece of the same metal, which, by a curvature, can be inserted into a second cup, in which is placed a plate of a different metal, suppose zinc, to which this wire is also attached. We have thus the two metals connected by a metallic arc, with fluid surrounding them. In the second cup is placed another plate of silver, at a distance from the zinc, which is connected with a plate of zinc in a third cup; and in this manner the series is prolonged, through a number of cups.

Volta communicated an account of his pile to the Royal

Society of London *. A number of experiments with it were soon made by the British chemists, and it was in the prosecution of these researches that the discovery was made of its agency in producing chemical effects. Mr Carlisle and Mr Nicholson, observing accidentally, that from a globule of water on the upper metallic piece of the pile, a small stream of gas arose, which had the smell of hydrogen, Mr Nicholson proposed to introduce wires, connected with the two extremities of the pile, into a tube filled with water, and they had the satisfaction of perceiving immediately a stream of gas to arise from the wire connected with the negative side of the pile, and the wire connected with the other appeared to be oxidated. On employing wires of a metal not easily oxidable, as platina, a stream of gas issued from each, that from the one being hydrogen, from the other oxygen †. These experiments were immediately extensively prosecuted.

Mr Cruickshank greatly facilitated the investigation by his invention of an apparatus, more convenient, and capable of being rendered more powerful than the pile. It is what is named the Galvanic Trough. It consists, Fig. 69. of a trough, of hard wood, in the sides of which are cut small grooves, at the distance from each other of from $\frac{1}{4}$ to $\frac{3}{4}$ of an inch, according to the width of the trough. Plates of two metals, generally of copper and zinc, not less than 2 or 3 inches, and usually of 4 or 6 inches square, are soldered together, and this soldered or double plate is inserted in each groove of the box, and fixed in it by a cement of resin and wax, so well applied that no liquid can pass through, taking care that the order in which they are inserted shall not be reversed, but that if the copper side of the double plate has been next to the extremity of the trough at which the insertion has commenced, the copper

* Philosophical Transactions for 1800.

† Nicholson's Journal, 4to, vol. iv, p. 179.

sides of all the others shall be in the same position, and the zinc side of the last plate shall therefore be opposite to the other extremity. The grooves thus filled by the metallic plates, being at a certain distance from each other, there are of course cells or cavities between them, and these are designed to contain the liquid by which the galvanism is excited, or they serve the same purpose as the moistened cards or pieces of cloth in the pile of Volta.

This arrangement is possessed of great advantages, compared with the pile. The surfaces of the two metals which are in contact, by being soldered, are prevented from suffering any chemical change, by which their conducting power would be impaired; and the cells containing so much liquid, the trough can be preserved longer in action than the pile; and the action from a given surface of metal is from the same cause more energetic. It is also more easily put in action, and kept clean.

Another mode of constructing the voltaic battery has since been introduced. By the plates of the two metals being soldered together in the old method, one of the surfaces of each being protected from the action of the liquid, contributes nothing to the effect. In the new mode the plates are not in contact, but are placed at a distance of half an inch, and are connected by a metallic arc. The trough is divided into cells by partitions of glass, the sides being rendered sufficiently close by the usual cement; or it is constructed of earthen ware, with partitions of the same material. The plates are introduced, so that the partition is interposed between them, and the arc above forms the communication; each plate in this state of connection is thus in a different cell, and each cell contains a plate of each metal unconnected, except by the medium of the liquid; the due order being observed, so that the series of zinc, copper and liquid is preserved. The arrangement is precisely similar to that of the *Couronne de Tasses*, described page 592, the form only being more

convenient and economical. The plates are sometimes hung at the proper distances from a rod, so that they can be raised from the liquid when it is wished to interrupt the experiment. This is an advantage, as avoiding an unnecessary expenditure of power, and also from another circumstance, that the action of the metallic plates is always most powerful at their first immersion, that it gradually diminishes, but is renewed by removal, and a new immersion. Mr Pepys has given the construction of a very complete apparatus on this plan*. These advantages are, on the other hand, in some measure counterbalanced by the circumstance, that in order that the plates may be easily introduced into the cells, it is necessary to place the partitions at a considerable width, and thus a large quantity of liquor is required: if a very extensive arrangement be employed, however, this greater distance at which the plates in each cell are placed, prevents spontaneous discharges from one to the other. With regard to the arrangement under either form, it does not appear that it has the advantage which was at first supposed to belong to it, that of affording from a given number of plates a double power, from the circumstance of both surfaces being acted on; its power is certainly far inferior to this, and perhaps does not much exceed that from the soldered plates; while, from the very circumstance of both sides of the metal being chemically acted on by the liquor, the action is sooner exhausted. It has the convenience, however, that the state of the plates can always be discovered, and that, if necessary, they can be easily repaired. This form of the trough is represented Fig. 68.

The metals used in constructing a voltaic series are generally zinc and copper, and these, on the whole, answer best; silver and zinc appear to furnish a more powerful combination, but the difference is not considerable. The

number of plates, and their size, must be regulated by the purpose to which the trough is to be applied. The wires for conducting and applying the galvanism should be of a metal not liable to chemical change ; those of gold or platinum have this advantage.

Different liquids are employed to fill the cavities of the trough, and differ much in power. With water, the effect is very inconsiderable ; with a solution of sea salt (muriate of soda) or of muriate of ammonia, it is much greater ; it is still more so with diluted acids, and these have the farther advantage, that they keep the surface of the plates clean, or at least remove very quickly any crust of oxide which would impede the excitation. Nitrous acid diluted appears to be most powerful. From the experiments of Mr Singer *, it appears, that when equal proportions of the three mineral acids to a given portion of water are employed, the most intense heat measured by the quantity of iron-wire melted in the galvanic circuit is produced by nitric acid, next to it by sulphuric acid, and least by muriatic acid ; the latter, however, exceeded the others in the length of time during which it retained its power. The extent of dilution requires to be different, according to the size and number of the plates, and according to the effect designed to be obtained ; heat and light are produced in the highest intensity, as the acid is less diluted, while to produce chemical decomposition, it may be more diluted ; and a stronger acid is required where a battery of large plates of no great number is employed, than where a battery of small plates of a much greater number is used. When the acid liquor is strong, the action of it on the metals is attended with so much effervescence as to be inconvenient. On an average, nitric acid may be diluted with 30 parts of water, muriatic acid with 20 or 25 ; sulphuric acid diluted with 25 of water acts powerfully, but

* Nicholson's Journal, vol. xxiv, p. 175.

its action soon ceases. A mixture of sulphuric and nitric acids in the proportion of one of the former to two or three of the latter, this compound acid being diluted with about 40 parts of water, excites powerfully, and for a considerable time, and is more economical than nitric acid alone. A solution of sea-salt, with the addition of a little muriatic acid may be used, where continuance rather than strength of action is required. Gay-Lussac and Thenard found that the mixture of salt and a diluted acid acts more powerfully than the diluted acid alone. The effects, which are purely electrical, displayed in the power of affecting the electrometer, are best obtained from a weak saline solution, and are excited even by water alone.

It has not been found, that those advantages which were expected from very powerful voltaic batteries are attained. Beyond a certain degree of energy various circumstances operate, which counteract the effect, or render it less capable of being applied to the purpose of chemical decomposition: the interposed liquid, in particular, is rapidly decomposed, so as to render the experiment difficult of management; its power, from the same cause, diminishes rapidly; and the state of electrical intensity is such, that unless the battery be very perfectly insulated, there is a loss of power. It had been supposed, that insulation of the galvanic apparatus is not necessary to obtain its effects, and in arrangements at a low state of intensity this is the case. But in very powerful arrangements, this insulation is required, and the experiments of Van Marum had shewn that it considerably augments the effect*. It is a curious fact, that removing the liquor from the cells when it appears exhausted, and again introducing it, causes a renewal of power.

Though the arrangement of two metals, with certain chemical fluids, be that generally employed, it is not the

* *Annales de Chimie*, t. xl, p. 305.

sole one from which galvanic electricity may be generated; and as illustrative of the theory of its production, some facts with regard to this require to be stated.

The combination of a single metal with a fluid evolves this power, as is discovered from the power of such a combination to excite contraction in the muscles of a prepared frog; but no accumulating series of this kind can be formed. A metal acted on by two different liquids affords an arrangement, the powers of which are augmented by repetition, though in different degrees, according to the nature of the liquids. If a series be formed of water, metal, diluted nitric acid, the excitation is evident, though not considerable. One similar in power is formed from the series, water, metal, sulphuret of potash; while from the series, dilute nitric acid, metal, sulphuret of potash, the production is much greater than from the other, as Davy ascertained*: he observed, too, that a piece of charcoal, in contact at one of its surfaces with water, at another with nitric acid, shews signs of electricity. A galvanic arrangement may be formed, even according to Volta, without the intervention of metal, of different kinds of animal matter.

The effects produced by the action of Voltaic Electricity are next to be stated.

In compound arrangements, the two extremities of the series are in opposite electrical states, that which commences with the more oxidable metal, the zinc, is positive, and that terminating with the other metal, the copper, is negative, the difference being greater according to the extent of the series. If a communication is established by a conductor, as a metallic wire, the discharge from the one extremity to the other takes place; and substances placed at the point of contact are acted on with a force proportional to its power.

* Philosophical Transactions for 1801.

The power thus excited passes through those substances which are conductors of electricity, and, in general, with the same differences of rapidity. Hence the metals are the best conductors of it; the power of charcoal, in this respect, is somewhat equivocal, as it is with regard to electricity; some pieces conducting imperfectly, while others are more perfect in conducting power. Plumbago is a conductor. Different liquids,—water, saline solutions, and others, all conduct it to a certain extent, as is obvious from their forming part of the galvanic circle in the trough or pile; but still they conduct it less readily than electricity; and substances which conduct electricity, as the dry cuticle, are scarcely pervious to galvanism. These differences appear to arise from the usual low state of intensity of voltaic electricity, and are not observed, therefore, when this intensity is sufficiently raised. Glass is a non-conductor.

Though the effects of galvanism on the living system are not chemical, yet, as connected with its general agency, it may be remarked, that a sensation similar, though not precisely the same with that from the electrical discharge, is felt when the two extremities of the battery, or conductors connected with them, are touched with the fingers wetted. If the battery is weak, it extends up the fingers; if stronger, it is felt at the wrist, or even to the shoulder, and from a very powerful battery the sensation is scarcely tolerable, and a sense of weakness is felt in the arms for a number of hours. Contractions of the muscles are at the same time excited.

In its transition from one conductor to another, especially when the conductor is an imperfect one, galvanism produces intense light. If the wire issuing from one extremity of the trough be made to touch the wire that comes from the other, at the moment of contact, a spark more or less vivid is excited. If the wire be made to touch a piece of plumbago, or well-burnt charcoal, which is connected with the opposite wire, the spark is more vivid; and if

each of the wires be terminated with small-pointed pieces of well-prepared charcoal, on bringing them into contact, the light excited is the most intense and pure which we can produce by any artificial arrangement ; if the trough is a large one, innumerable rays dart from the point of contact, and continue to do so while the contact is preserved. This galvanic light seems principally to arise from the accumulation of the galvanic electricity, or the restoration of the electric equilibrium from the two different states, by the contact of imperfect conductors. It does not arise from combustion ; for it is attended with scarcely any waste of the metal or charcoal, and it can also be excited, though with diminished splendour, under water, oil, alkohol, and other fluids, and in gases not capable of supporting combustion. It was supposed that the galvanic spark cannot be exhibited like the electric spark, when the conductors are at a sensible distance, but that the light is produced only when they are in contact. When a very powerful battery, however, is employed, the spark can be taken at a distance. Mr Children having placed two wires in air dried by potash, found a spark appeared when they were connected with a battery of 1250 four inch plates, on bringing their extremities within the distance of $\frac{1}{16}$ of an inch ; and a more diffused, but very vivid light, may also be produced at a considerably greater distance, in a rarefied elastic medium.

Galvanic electricity may also be applied so as to excite very intense heat. The communicating wires become hot when the circuit is completed. If leaves of gold, silver, copper, tin, and other metals, be suspended from a wire connected with one extremity of the trough, on applying to the edges of them a metallic plate, connected by a wire with the other extremity, such a heat is excited at the point of contact that the metals enter into a vivid deflagration, with the emission of different coloured lights, and they are found to have suffered that chemical change,

which is analogous to combustion. Iron-wire burns, with the emission of numerous vivid sparks. The inflammable gases are kindled by the galvanic spark when sufficiently strong, if they are in contact with the air; or, if mixed with oxygen, they explode on its introduction. The heat excited, independent of combustion, is shewn by placing a wire in water, forming a part of the circuit, when the water is soon made to boil. The metals also, iron or platina wire for example, can be ignited, and even fused, independent of their combustion, by the wire being stretched between two rods, connected with the extremities of the battery. By the powerful battery at the Royal Institution, consisting of 2000 double plates of four inches square, the least fusible metals, as platina, were instantly melted, and the most infusible earths, and earthly minerals, as argil, zircon, magnesia, lime, quartz, &c., were fused. By a battery constructed by Mr Children, of plates, the largest that have been used, (each plate being six feet long by $2\frac{1}{2}$ feet broad, 20 zinc plates being inserted in separate cells, with wooden partitions, with two copperplates in each cell, the whole connected by leaden straps, and excited by a mixture of sulphuric and nitric acids diluted with from 20 to 40 parts of water,) $5\frac{1}{2}$ feet of platina wire 0.11 inches in diameter were raised to a red heat visible in day light, and $8\frac{1}{2}$ feet of platina wire 0.044 inch in diameter suffered the same change: a bar of platina 2.25 inches long, and one-sixth of an inch square, was ignited throughout, and fused at the extremity; some of the most refractory of the metallic oxides, as those of tungsten, uranium, titanium and cerium, were fused, and oxide of molybdena was fused and reduced; iridium was melted, and iron in contact with diamond was converted into steel. The effects produced by voltaic electricity were found, by the results obtained by this powerful apparatus, not to be directly conformable to those produced by the direct communication of heat. Thus the facility and extent of igni-

tion were very different in the different metals, a wire of one metal being ignited, while a wire of the same diameter of another metal was not by the same discharge; the order in facility of ignition was that of platina, iron, copper, gold, zinc and silver, a difference which Mr Children supposed to arise from the difference of conducting power with regard to electricity, the effect of ignition being inversely as the conducting power, and silver, therefore, according to this opinion, being the best conductor. Too great a resistance, however, to the transmission may oppose the effect, and to this probably it may be owing that some substances, as quartz, ruby and sapphire were not melted, though others equally refractory from heat directly applied, as molybdena, were easily fused *.

No satisfactory theory can be given of this evolution of heat by galvanic action. It is evidently connected with the neutralization of the two opposite electricities by the contact of the wires from the positive and negative extremities of the battery, and the consequent restoration of the electric equilibrium. But how this should produce heat is not apparent. Whether temperature can be directly elevated by electricity, or whether the transmission of electricity may cause a similar transmission of caloric from the matter composing the circuit to the point at which the discharge is effected, cannot be determined. From the consideration that heat is thus capable of being excited, and that apparently for an unlimited time, by electric excitation, it has been supposed that the heat produced in chemical action may arise from changes induced in the state of electricity connected with that action. But this rests on assumptions vague and uncertain, and the subject admits at present of no satisfactory conclusion.

The most important agency of voltaic electricity is that by which it gives rise to chemical decomposition. Of all

* Philosophical Transactions for 1815.

the forces which subvert combination, it is the most energetic; and as by enlarging the apparatus producing it, it may be accumulated to any degree of intensity, it admits of being applied in a high degree of power, and accordingly decompositions have been obtained by it, which have not been effected in any other mode.

The decomposition of compounds by the action of this force is obtained by placing the body submitted to it in connection with one extremity of the voltaic battery, and applying a metallic wire in communication with the other extremity. The elements of the compound are separated, and can be obtained in their insulated form. If platinum wires, for example, connected with the two extremities, are placed in water, the elements of the water are immediately disjoined, and, as they are gaseous bodies, assume the elastic form, and are disengaged. Other compound liquids are decomposed with equal facility; and even solids, when their conducting power with regard to electricity is favoured by humidity, and a powerful battery is employed, suffer decomposition.

These decompositions presented considerable difficulties with regard to their theory, from the singular phenomenon observed in them, that the elements of the compound decomposed are not evolved together, but that one is evolved at the wire connected with the one extremity of the battery, and the other at the wire connected with the opposite side; and this even when the wires are placed in separate portions of the compound, provided these are connected by a substance, such as water, which is a conductor of galvanism, and capable of transmitting the elements of the compound. To account for this, as applied to particular cases, different hypotheses were proposed. Cruickshank suggested the opinion, that the galvanic influence might convey the principles of the decomposed compound to a distance, so as that they should appear at

different parts. And the law with regard to this was more clearly established by Berzelius and Grotthus.

In a series of experiments by Hisinger and Berzelius *, it was shewn, that a number of neutral salts, placed in the galvanic circuit, by wires connected with the two extremities of the galvanic battery being placed in their solutions, suffer decomposition, as had been indeed before known ; and that when wires are employed, to which either of the elements of the salt have an attraction, a combination of this element with the matter of this wire is formed at the one side, and at the other side the other element is evolved pure ; or if the wires were of a metal, gold for example, to which these elements have in general no sensible affinity, then they are evolved in their pure form. In both cases, it was observed, that the acid of the salt was collected at the positive side, and its base, whether alkali, earth or metallic oxide, was found at the negative side. They drew from these experiments the general conclusions, that “ when electricity passes through a liquid, the principles of that liquid separate, so that some are collected around the positive pole, the others around the negative ;” and “ that the principles which collect around each pole have a certain analogy ; combustible bodies, alkalis, and earths pass to the negative side ; oxygen, acids and oxidated bodies pass to the positive.” They also demonstrated the exertion of the force by which these effects are produced at a distance, and the consequent transfer of matter from one pole to the other. A syphon, the curvature of which was perforated to allow the gases to escape, and through the extremities of which, iron wires were inserted, was filled to two-thirds, on one side with a solution of muriate of ammonia, and on the other with sulphate of potash, and a communication was formed between these by distilled water ; at the end of 28 hours, the liquor in

* Annales de Chimie, tom. li, p. 167.

the negative side, which contained the sulphate of potash, had become alkaline, and contained also ammonia; while the liquor at the positive side, which contained at first only muriate of ammonia, now contained sulphuric acid. It appeared, therefore, that the salt at the negative side had yielded part of its acid to the salt at the positive, and this again had yielded part of its alkali to the other. And these portions of acid and alkali had of course been conveyed through the distilled water. In another experiment, the syphon was filled on the one side with muriate of lime, and on the other with water; the acid passed to the positive side, the lime to the negative side.

Grotthus announced a similar principle, as affording the explanation of the decomposition of water and other substances by galvanism,—that the one pole of a galvanic series attracts certain elements, while the other pole attracts others, oxygen being attracted to the positive, hydrogen and metals to the negative side; and he stated a number of facts with regard to these decompositions, to elucidate this principle: Sulphuric acid, for example, deposits sulphur, and nitric acid becomes nitrous, at the negative side, while at the positive they appear to be surcharged with oxygen; and if the positions be reversed, they return to their former state. Metallic salts become more highly oxygenated at the one pole, and less so at the other, as is very well shewn among other examples in sulphate of iron, which at the positive side passes to the state of red sulphate, so as to give a deep blue precipitate with prussiate of potash, while at the negative side it gives the less highly oxidated precipitate of a greenish white colour*.

Sir H. Davy gave an extensive series of experiments, varied with much ingenuity, so as to place the facts connected with these decompositions in a striking point of

* *Annales de Chimie*, t. lviii, p. 64, or *Philosophical Magazine*, vol. xxv, p. 330.

view. He employed two vessels of glass, or, as being less liable to be acted on, of agate, or of gold, connected by a few fibres of the mineral substance named asbestos, moistened with water, placing in each a solution of a compound salt, and inserting in the one a wire from the positive side of a voltaic battery, and a wire from the negative side in the other. In a short time, the principles of the salt are separated; and at length all the acid is collected in the one vessel, and its base in the other; each being conveyed by the medium of the moistened asbestos. If the solution were placed in one vessel, and distilled water in the other, either the acid, or the base of the salt, might be transferred to the distilled water, according as it was connected with the positive or the negative side of the galvanic trough, the acid passing to it if it was connected with the positive side, and the base, if with the negative side. In this way, even metals could be transferred, as silver, from nitrate of silver, or insoluble earths, as magnesia, from sulphate of magnesia. When the vessels themselves were composed of substances susceptible of decomposition, the same separation of elements was effected, though more slowly. This effect was obtained from cups of sulphate of lime, sulphate of barytes, &c. Even glass is liable to this decomposition. And such is the force of this agent, that the most minute portion of a substance thus acted on by either of the wires is collected around it,—a circumstance which has often been the source of deception in galvanic experiments, with regard to the apparent formation of new products. These decompositions are also, if the action is continued sufficiently long, always complete.

So completely is the matter thus conveyed by the galvanic influence protected by it, that it may be transmitted through a substance to which it has a chemical affinity, without being retained. Thus, if instead of two, three vessels are connected, a solution of a salt, such as sulphate

of potash, being placed in the first, with the negative wire immersed in it, in the middle vessel a solution of ammonia, a substance having a strong attraction to sulphuric acid, and in the third, water, a wire from the positive side of the galvanic battery being immersed in this water, in 5 minutes, when a battery of 150 pairs of plates was used, acid was found collecting around the wire in the water; it had therefore passed through the ammonia without the affinity of this being sufficient to arrest it. When the disposition was reversed, and the saline solution connected with the positive side, the water with the negative, and an acid placed in the middle, the alkaline base was conveyed through the interposed acid, and collected in the pure water. The same result was obtained in operating on a number of other salts; and, in fact, this is merely prolonging the distance at which the forces producing these effects are exerted, since, if the first attraction—that between the principles of the salt, could be overcome by these, the other affinity, that of the interposed liquid to the conveyed substance, must also be suspended. Where a strong force of cohesion, however, interfered, the substance was intercepted; thus, sulphuric acid was not transmitted through solutions of barytes or strontites; nor these earths through sulphuric acid.

It was inferred as a general expression of these facts by Sir H. Davy, “that hydrogen, the alkaline substances, the metals, and certain metallic oxides, are attracted by negatively electrified metallic surfaces, and repelled by positively electrified metallic surfaces; and contrarywise, that oxygen and acid substances are attracted by positively electrified metallic surfaces, and repelled by negatively electrified metallic surfaces; and these attractive and repulsive forces are sufficiently energetic to destroy or suspend the usual operation of elective affinity*.” The more

* Philosophical Transactions for 1807.

strict expression of the fact is that which had been stated by Berzelius, that when electricity passes through a liquid, its principles separate, so that some are collected around the positive pole, the others around the negative, oxygen, acids, and oxidated bodies passing to the positive, combustible bodies, alkalis, and earths, passing to the negative. Whether this is by the exertion of attraction, or of repulsion, or of both, to the respective elements at the several poles, is a farther question, which may be subject of discussion, and which cannot be considered as determined with any certainty *.

* In this conveyance of the elements of a compound from one distant point to another, there is less difficulty in conceiving of the effect where the continuity of the substance acted on is preserved between the two wires, or where a substance is interposed in which they are capable of being diffused. But it has been affirmed, that when the two portions of the compound are connected so as to complete the galvanic circuit by a solid body, which it cannot be supposed that the elements of the compound are capable of penetrating, as a metallic wire, the usual decompositions are effected. Ritter, in particular, stated, (*Nicholson's Journal*, 4to, vol. iv, p. 512,) that when portions of water are thus put in separate tubes, the wire from the positive side being in one tube, and that from the negative in another, on establishing a connection between the water in these tubes by a metallic arc, the usual appearances are presented, oxygen is evolved at the positive wire, and hydrogen at the other. And from this he concluded, that as these substances cannot be conveyed through the metal, the results must arise merely from the communication of electricity to the different portions of water; that water, therefore, is a simple body, which takes the forms of oxygen and hydrogen according to its electrical states.

The appearance stated by Ritter I found is a deception. The connecting wire does not merely form a medium of communication, but passes into an electrical state, so that the one extremity of it, that opposed to the negative galvanic wire in the

With regard to the mode in which these effects are produced; there is some uncertainty. The general result of

one tube, becomes positive, and the other extremity opposed to the positive galvanic wire becomes negative. Hence at these the same actions proceed as at the extremities of the galvanic wires: hydrogen, for example, in the decomposition of water, being given out at the extremity of the connecting wire opposite to the wire from the positive side of the galvanic battery which is giving out oxygen, and oxygen being evolved at the other extremity of this connecting wire opposite to the negative galvanic wire at which hydrogen is disengaged. The same thing happens in the decomposition of a neutral salt. If portions of its solution, coloured with a blue vegetable infusion, be put in separate tubes connected by a metallic wire, on placing in the one a wire from the positive side of a galvanic battery, and in the other a wire from the negative side, the liquor becomes red around the end of the positive wire, from the acid of the salt being attracted to it, but it also becomes green around the extremity of the connecting wire in that tube; and again it becomes green around the negative wire in the other tube, from the alkali being attracted to it, but it becomes red also at the extremity of the connecting wire in that tube. The portions of acid and of alkali, therefore, corresponding to those which are attracted to the positive and negative galvanic wires, are merely attracted to the extremities of the connecting wire, these extremities being in states of electricity the reverse of those of the galvanic wires to which they are opposed. The passing of the connecting wire into this state is an example of electricity by induction or position. It is known, that if an insulated wire *a* be in one electrical state, if another wire *b* be opposed to it in the same position at some distance, its extremity opposed to *a* will pass into the reverse state. From the low state of intensity in which electricity exists in the galvanic apparatus, water is a medium with regard to it nearly as atmospheric air is to electricity in its common form: it allows, therefore, of this state of electricity by induction being established in the connecting wire, and hence the actions which are exerted at its two extremities corresponding to those of the positive and negative galvanic wires.

decomposition has been conceived to depend on different electrical states being impressed on the elements of the compound, one element, in all cases, in consequence of some peculiar relation of bodies to electricity, being disposed to assume the one state, the other the other; and these states being assumed, each element, in conformity to the usual laws of electric attraction and repulsion, that bodies in different electrical states attract and in the same electrical states repel, will be attracted to the pole, which is in a different electrical state, and repelled from the other. The column of Volta, it was observed by Grotthus, is an electrical arrangement, every element of which, that is, every pair of plates, has its negative and positive poles. This suggests the idea that it may establish a similar polarity among the elementary particles of water submitted to its action. If a subversion of the natural electricity of the hydrogen and oxygen, the two elements of water, take place in such a manner, that the former acquires the positive and the latter the negative state; it follows, that the pole which is negative will attract the hydrogen by rejecting the oxygen, while that which is positive will attract the oxygen by rejecting the hydrogen; each therefore is acted on by an attractive and by a repulsive force, of which, the centres of action are reciprocally opposite, which determine the decomposition of the water. The same polarity will be established in the elementary particles of any other liquid acted on by the same forces, and give rise to similar decompositions, and the evolution of the elements at the respective poles*.

To explain the mode of conveyance of the elements, Grotthus supposed that there might be successive decompositions and recompositions of the compound between the two poles; in water, for example, the particle at each wire

* *Annales de Chimie*, t. lviii, or *Philosophical Magazine*, vol. xxv.

may be decomposed ; the one element may be disengaged, and the residual element may attract a corresponding portion of the other from the next particle, and thus by a series of successive decompositions and recompositions, each may be brought to the wire to which it is attracted and evolved. It is also possible that the effect may be produced in a more simple manner. A particle of the compound may be decomposed at each wire, and the element repelled from it may, by this repulsion, and the corresponding attraction at the opposite wire, be brought to this wire. Repulsion and attraction are exerted in common electricity between bodies suspended in atmospheric air at considerable distances ; and from the low state of tension in which electricity exists in the galvanic apparatus, water appears to be as imperfect a conductor with regard to it as atmospheric air is to electricity in its common form. It may, therefore, allow these forces to operate in a similar manner, so that if the elements of the compound are separated at the two poles, they may be attracted or repelled through the intervening space without successive combinations and decompositions.

With regard to the principle, that the subversion of the power of chemical attraction, and the consequent decomposition of bodies by galvanism, is owing to the electrical states communicated to their elements, in consequence of which the one is attracted to the one pole, the other to the other, it appears at first view probable ; there exists indeed no other apparent cause, and it might be supposed to be almost necessarily inferred from the phenomena. Yet there is one difficulty with regard to it. Admitting different bodies to receive different electrical states, this must strengthen their mutual attraction, (bodies in different electrical states attracting each other,) and hence must resist their separation. To obviate this it has been supposed, that the communication is not made to both elements but to one of them ; but there is an obvious improbability in such a

supposition, and even were it admitted, it would follow, as Mr Donovan has justly remarked, that from one of the wires at least, that which is in the same electrical state with that in which the elements of the compound are, both must be repelled, while they will both be attracted to the opposite wire.

To obviate the difficulty, it is only necessary to suppose, that while the elements of a compound placed in the voltaic circuit receive the different electric states, one becoming positive, the other negative, they do not receive these states to the same degree of intensity as that which exists at the galvanic poles ; and that this is the case, is probable, from the consideration that the compounds decomposed by galvanism are all imperfect conductors compared with the metallic surfaces communicating the electric states : there must therefore be some accumulation of the galvanic power at the points where the communication takes place, and therefore higher states of electrical intensity will be produced. These will therefore operate with more power, and overcome the attraction arising from the difference in the electric states of the elements of the compound, and even the chemical attraction which is exerted between them. Their separation will thus be produced, and each will be repelled from the wire which is in the electric state, the same as that in which it exists, and be attracted to the other.

It has also been supposed, that the separation of the elements of a compound under galvanic action may arise from increase of temperature at the respective poles, since the discharge of electricity from one body to another is attended with this effect ; and that in consequence of the separation, the different electrical states may be assumed, the one element becoming positive, the other negative, whence the repulsion of each from the pole in the same state, and its attraction to that in the opposite state will take place. An hypothesis of this kind was proposed by

Dr Maycock *; but its leading assumption, that the decomposition arises primarily from elevation of temperature, is doubtful.

From the influence of electric attraction and repulsion in producing these decompositions, the idea has even been suggested, that chemical attraction may be a modification of electrical energy. If in two bodies, the particles of each are in different electrical states, and these states sufficiently exalted to give them an attractive force superior to the power of aggregation, a combination between them, more or less intense, may be formed. From different degrees of electrical energy in two bodies, in relation to a third, decompositions by what is called elective affinity may be produced; or there may be such a balance of attractive and repellent powers as to produce a ternary compound. The effect of heat in promoting combination or decomposition may often depend on its exciting electrical energy; and the elevation of temperature, and production of light, so frequently attending chemical action, may depend on the changes attending the electrical states, since such changes are accompanied with the evolution of heat and light. This view of the subject was brought forward by Sir H. Davy †, who, in support of it, farther stated experiments, from which it appeared, that bodies which combine chemically also act electrically: they acquire different states of electricity on their separation, after they have been in contact with each other. Thus sulphur and metals after contact, and especially when heated, exhibit different states of electricity, the sulphur being positive, the metal negative. Dry acids, such as the oxalic and boracic, when touched with a plate of copper, become negative, the copper becoming positive; on the contrary, the metal becomes negative when applied to the earths, and the earth positive; and a dry acid, as the oxalic, from contact with

* Nicholson's Journal, vol. xxix, p. 28.

† Philosophical Transactions, 1807, 1808.

a dry earth, as lime, becomes negative, the earth becoming positive. The objections to this hypothesis by Mr Donovan * and Dr Maycock †, are ample and conclusive. It cannot be assumed that bodies are naturally in different electrical states, the uniform tendency is to the state of electric equilibrium, and the positive and negative are forced states dependent on the operation of external causes. All that can be assumed is, that bodies may be peculiarly disposed to receive these states; some having a tendency to pass into the one, others into the other, if they are submitted to operations exciting them, an assumption insufficient to maintain the hypothesis, since it requires the condition that they actually are in such states. And even if this were granted, they must, when they unite, lose this difference of state, the electric equilibrium be established, and their mutual attraction cease, so that no permanent combination could be formed. Mr Donovan has also shewn, in opposition to this hypothesis, that bodies in opposite states of electricity do not combine when presented to each other, and that bodies in similar states combine with as much force as if in different states; and he has added, in a late publication ‡, some other facts and arguments, and some just observations, in reply to what Sir H. Davy had urged in support of his opinions.

Berzelius has advanced views similar to the preceding, forming what he has called the electro-chemical theory, founded on the principle, that electrical polarity in the particles of bodies is the force on which their chemical affinities depend, and on the laws supposed to be inferred from experiment, that all bodies in which the changes can be observed are positive with regard to oxygen, which is of course itself negative, and that, in relation to each other,

* Philosophical Magazine, vol. xxxvii, p. 227.

† Nicholson's Journal, vol. xxix, p. 12.

‡ Essay on Galvanism, p. 196.

of two bodies, that which has the strongest attraction to oxygen becomes positive, the other negative. His speculations on this subject * are not less vague and hypothetical, and the precise nature of the relation of electrical energy to attraction, and of its operation in chemical action, still remain problems to be solved.

A singular and important fact connected with the chemical changes produced in bodies by galvanic electricity, is the suspension of their chemical properties when they are brought into electrical states. Thus the power of an acid, it has already been remarked, was found by Davy not to be displayed in reddening the colour of litmus when transmitted through it by the power of a galvanic battery acting in the decomposition of a compound salt, but appeared only when it was collected around the positive wire. And an alkali in like manner did not exert its property of changing the colour in its progress through the infusion, but only when collected at the negative side.

In the different effects which arise from voltaic electricity—that of exciting heat and light, of causing chemical decomposition, and of displaying the usual electrical phenomena, a peculiar relation with regard to each exists in the construction of the voltaic arrangement. That the power of the apparatus should increase with the number of plates is what is to be expected, and, accordingly, this increase of power was found by Messrs Wilkinson and Cuthbertson, and by Mr Singer, to be in direct proportion to the number of plates employed; so that if a given number produce a certain degree of effect, twice the number produce twice the effect †. It may also be expected, that an enlargement of the surface will increase the effect;

* *Memoir, Journal de Physique*, t. lxxxiii; or *Abstract of it, Nicholson's Journal*, vol. xxxiv.

† *Nicholson's Journal*, vol. xxix, p. 29.

and this is the case to a certain extent. A singular fact, however, was discovered by Thenard, Fourcroy and Vauquelin, that an increase in the number of plates, without a proportional increase in their surface, does not augment equally all the effects ; but that a different law is followed in the increase of the power of igniting the metals, and in that of giving the shock to animals, or decomposing chemical compounds. The power of igniting the metals depends principally on surface ; so that a few large plates, as twelve of 12 or 20 inches square, cause them to burn with the greatest brilliancy ; while the same plates, divided into 48, produce an inconsiderable effect. On the other hand, the power of giving the shock, and of producing chemical decompositions, is rather dependent on number ; the twelve large plates give a feeble sensation, or decompose water slowly ; while, if cut down so as to form an arrangement consisting of 40 or 50 small plates, their powers with regard to these effects are greatly enlarged *. This result has been confirmed by subsequent researches. Mr Children constructed a battery of 20 pairs of plates of zinc and copper, each plate being four feet high by two feet broad. This charged with a mixture of nitrous and sulphuric acid diluted with water, produced a heat so intense as to fuse 18 inches of platina wire $\frac{1}{5}$ of an inch diameter ; but it was feeble in producing chemical decomposition, and gave no sensible shock. He next employed a battery of 200 pairs of plates each two inches square ; and with this, compounds the most difficult of decomposition were readily decomposed †.

From these facts it has been stated in general terms, that the power of igniting the metals is in the ratio of surface affording galvanic electricity, while the other effects are in proportion to the number of plates. Ritter investiga-

* Journal de l'Ecole Polytechnique, tom. iv, p. 291.

† Philosophical Transactions for 1809.

ted the subject with more precision, and his results, if accurate, are important.

“ A. He constructed a pile with 1000 plates of copper, zinc, and pasteboard moistened with a solution of common salt in a decoction of litmus and galls, this conducting better than a simple solution of common salt. He divided these into ten columns, and connected them, in the usual way, into a single pile. He hung on the upper plate (which was zinc) a leaf of gold, and began by including 100, then 200, and 300 plates in the conducting circle. The maximum of combustion he determined by the magnitude of the perforation which the blunt extremity of an iron wire from the negative side burnt in gold-leaf attached to the *plus* side. This maximum, he found to be between the 200 and 300 plates; beyond these the spark, to external appearance, for some time seemed greater, but it continued to lose its energy, until all the 1000 plates taken together scarce yielded a trace of true combustion, and the effect of the spark on the gold-leaf appeared to be only mechanical.

“ The *chemical effect*, which was determined by the quantity of gas evolved from the decomposition of water, increased from 100 plates, pile for pile, and usually at 600 plates reached its maximum; 700 or 800 plates operated more weakly, and all the 1000 plates considerably weaker than the 400.

“ With respect to the *shock*, its energy increased to 1000, and then it required a strong resolution to overcome the feeling, so that its maximum, with the above arrangement, seemed to be beyond 1000. From piles of 1500 plates, the shock was insupportable; but still no maximum could be observed.

“ B. He erected a pile of the same magnitude, with a simple solution of sea-salt. He found the maximum of combustion at the 200th plate. The maximum of the *che-*

mical effect was at 500 : 1000 was not more powerful than 300. No maximum of the shock was observable.

“C. With a pile of 2000 plates of copper, zinc, and cold concentrated solution of sal-ammoniac, the *spark* had its greatest energy between 600 and 800 plates, and from this began again to diminish. The *maximum of chemical action* was not to be observed within 2000 plates. It was supposed to be at 4000 or 6000 plates. No *maximum of the shock* was observed. It was impossible, even when the hands were dry, to bear the shock of 2000 plates.

“D. With a pile of 1000 plates, the pasteboard being moistened with well-water, a maximum of the spark was not accurately discoverable, but was supposed to be at 100; the maximum of chemical effect was above 100 plates; the maximum of the shock between 600 and 700; at 1000 the sensation was weaker. If the hands were wetted with a solution of common salt, the maximum of sensation was between 500 and 600; or with a solution of sal-ammoniac, between 300 and 400 *.”

It thus appears, that in the production of all these effects, a peculiar relation exists with regard to the extent, and the repetition of metallic surface in a voltaic series. The power of affecting the living system is dependent chiefly on repetition, that is, on the number of metallic plates, so that increasing the number adds to this effect; that of producing ignition or combustion depends principally on surface, so that increasing the number without increasing the surface is soon attended with a diminution of energy. The power of producing chemical decompositions is in relation to number and surface intermediate between these. But in all of them, a certain proportion between number and surface gives the maximum, and increasing either indefinitely is accompanied by a diminu-

* Gilbert's Annalen der Physik.

tion of power. If both be increased, preserving the proper proportions, the power may probably be indefinitely increased.

The theory of these differences probably is, that a peculiar state of intensity of galvanism is required for the production of each of these effects. The quantity of electricity generated in the apparatus will be proportional to the surface acted on, but its state of intensity is produced by its accumulation, and will therefore be regulated by the quantity of imperfect conducting, compared with perfect conducting matter in the arrangement. The liquid interposed between the metallic plates is the less perfect conducting matter: the repetition, therefore, of the metallic plates, the absolute surface remaining the same, forms an arrangement in which the imperfect conducting matter is most abundant, in which there is the greatest resistance to the evolution of the electric force, and in which therefore it will acquire the highest state of intensity. Now, a considerable intensity is requisite to enable the electricity to penetrate the animal membrane, which it must do to excite sensations or contractions, this membrane being an imperfect conductor. At a lower intensity, it will penetrate liquids, and act in decomposing them, observing a certain ratio with regard to this, according to the conducting power of the liquid; the less perfect the conducting property is, the effect in producing decomposition being more dependent on number. And metals are conductors so perfect, that in the lowest state of intensity it will penetrate them; the repetition therefore in the galvanic apparatus is less requisite; and the effects will be in a great measure proportional to the quantity generated. Hence the cause of the peculiar relations of number and surface to those different effects: the extent of surface giving quantity, and the repetition of surface in the series or number increasing the intensity of power. In conformity to this, it was found by Van Marum, that the intensity of the galvanic power

from a given number of plates is the same, whatever may be their size, though the quantity must be different. And Mr Children found, that electrical intensity was so low in a battery of large plates, that the gold leaves of the electrometer were not affected, while the battery with small plates caused considerable divergence; and in a battery of still larger plates, which excited the most intense heat, no charge could be communicated from it, in its most active state, to the Leyden phial.

The state of electrical intensity in the voltaic apparatus must also be varied, (the plates being the same in number and size,) according to the liquid interposed between them, those liquids which are less perfect conductors being favourable to its accumulation, though by retarding its discharge they may be least fit to promote its chemical action. This is accordingly the case: A battery of 24 plates, of a certain size, it is observed by Gay-Lussac and Thenard *, will, when excited by an acid, decompose potash, a proof of its great chemical energy; while a battery even of 600 plates will not be sufficient for this, if excited only by water, or even by a solution of sulphate of soda, though the latter will be in a higher state of electrical tension than the former. And as acids are better conductors than neutral saline solutions, while these are superior to pure water, these differences may be ascribed to this difference in conducting power. Different liquids differ much, therefore, in producing from a galvanic battery the different effects. When charged with an acid, more or less diluted, it is extremely powerful in producing heat and light; but its power of decomposing water and of giving the shock is not proportionally great. The last power seems to be nearly equally produced, when the battery is charged with a solution of a neutral salt. And from the experiments of Gay-Lussac and Thenard, it appears, that

* *Recherches Physico-Chimiques*, t. i.

though the decomposition of water is effected more powerfully with a diluted acid than with a solution of a neutral salt, yet the power of the battery in this respect is greater when these are combined, when along with the acid a quantity of salt is dissolved in the water.

On the same principle is to be explained the fact, that the facility of being acted on in a body subjected to galvanic action is much dependent on its conducting power. This is shewn with regard to water. When the wires from a galvanic battery are immersed in it, the disengagement of gas from the decomposition of the water is more abundant when the water holds dissolved a little saline matter, and still more when it is acidulated than when it is pure; this impregnation adding to its conducting power, and favouring therefore the communication of the electrical energies from the wires. In water entirely free from saline matter, the decomposition is extremely slow. And when the substance to be decomposed is an imperfect conductor, a battery composed of a large number of plates will be more powerful in producing the effect than one of a smaller number of larger size, while, if it is a better conductor, a battery of the latter kind may decompose it with nearly as much facility as the former. In Mr Children's battery of large plates, though the most refractory metals were fused, other substances less powerful conductors, such as some of the earths, were not melted, while they were melted by the powerful battery of the Royal Institution, which consists of a greater number of plates of smaller size.

A singular voltaic arrangement, the operation of which probably depends on the same principle, has been constructed by De Luc *, in which there appears to be an entire separation of electrical and chemical powers; at least while the former are considerable, the latter are not sensibly exerted. It consists of discs of zinc and fine tin

* Nicholson's Journal, vol. xxvi, p. 242,—vol. xxvii, p. 81.

or copper foil, with paper interposed between each pair of plates, or, what succeeds better, paper coated with copper leaf, (Dutch gilt paper,) applied to zinc. This instrument, the Electric Column as it has been named, very sensibly affects the electrometer, and charges a jar. But it does not decompose water, nor produce any chemical effect whatever. Mr Singer constructed it with some important modifications, introducing in particular two discs of paper between each pair of metals. A series of 1000 pairs of plates thus constructed, each having a diameter of five-eighths of an inch, causes the gold leaves in an electrometer to diverge at intervals of a second or two, and gives a charge to a Leyden phial capable of exhibiting a spark. Twenty of these columns being connected, constituting a series of 20,000 pairs of silver and zinc, the power was such as to affect pith-ball electrometers, causing them to diverge one or two inches; on bringing wires from the extremities, sparks were exhibited, a coated jar instantly received a charge, and in ten minutes became so powerful as to give a strong shock. But even in this state of activity it did not cause decomposition in any saline compound, or give any indication of any other chemical effect. Zamboni constructed a similar arrangement in a different form, employing discs of silvered paper with a thin layer of oil or a solution of honey and black oxide of manganese, coating the column with melted sulphur, and inclosing the whole in a glass tube hermetically closed. Electricity is constantly generated in this apparatus. It continues its operation for a number of weeks, and has even remained active for two or three years, and by the movement it communicates has been made to keep a pendulum in motion, or to strike a chime of bells. The theory of the instrument is not well understood. Electricity seems to be generated in it in small quantity, but is brought to a high state of intensity, and its peculiarity consists in the movement of electricity through the

series being much less rapid than in the common voltaic arrangements. Though apparently free from all liquid, it has been supposed that its effect depends on the hygrometric action of the paper discs ; hence it has been affirmed to be affected by the hygrometric state of the atmosphere : it has also been stated to be affected by temperature, and by the oxygen of the air ; while all these results have been denied by others*.

It remains to consider the theory of the production of Galvanism ; and the first question that occurs with regard to this is, What is the nature of this power ? Is it the same with electricity ?

In their properties they have a near resemblance. They act in a similar manner on the living system, producing sensation and muscular contraction. Galvanism in its transition from one matter to another is like electricity highly luminous ; like it, too, it produces intense heat, and is thus a powerful agent in occasioning chemical combination and decomposition. The conductors of the one are in general conductors of the other, while substances which refuse a passage to electricity are impervious to galvanism. Their connection is still more intimate. Volta observed, that on applying two metals to each other, an arrangement from which galvanism is produced, the one becomes positive with regard to electricity, the other negative. After the invention of the pile he found that its two extremities are in different electrical states—that connected with the more oxidable metal of the arrangement,—the zinc in the one generally employed being *plus*, that with the other *minus* ; the electrometer by contact with a wire connected with either extremity is affected, the effect of positive

* Nicholson's Journal, vol. xxxv, xxxvi. Philosophical Magazine, vol. xlv, xlv. Annales de Chimie et Physique, tom. ii.

electricity being communicated from the one, negative electricity from the other. A weak electrical charge can even be given to a coated jar, or to an entire battery, by forming a connection with the extremity of a galvanic pile. Volta found, that not only a Leyden phial, but a large battery, may be charged in the twentieth part of a second, and nearly to the same intensity as in the pile itself; and that such a charged battery gives sensible shocks *. Van Marum and Pfaff made the experiment on twenty-five jars, which they charged first separately, then a few at a time, and lastly all together. When the zinc was at the top of the pile, and the wire from it connected with the inside of the jar, the electricity of the inside was positive; and they found, that the single jars or the batteries were charged to the same degree of intensity as the pile or portion of the pile which they employed. The shock communicated from the charge made from twenty pairs of plates was inconsiderable; that from forty was felt at the wrists, and from sixty at the elbows. On comparing with these the effects of the common electrical machine, consisting of a plate of glass 31 inches in diameter; it appeared that a single momentary contact of the conductor did not give a charge to the battery, capable of being discovered by the electrometer; six of these contacts gave a charge of the same intensity as that from one contact of the pile. The shocks given by the battery, from contact with the pile, and contact with the machine, were perfectly alike, provided the intensities were the same †.

The differences which have been observed between electricity and galvanism, are principally that the galvanic power does not penetrate imperfect conductors, as the skin, charcoal, water, and other liquids so easily; and hence the

* Nicholson's Journal, 8vo, vol. i, p. 140.

† Memoir of Van Marum, Nicholson's Journal, 8vo, vol. i, p. 173.

galvanic apparatus does not require such perfect insulation as the electrical; and that its chemical action is more energetic, compared with its electrical energy, than in electricity evolved by friction. These differences are accounted for, as was suggested by Mr Nicholson *, on the principle that galvanism is electricity in a stream of great tenuity, while electricity from friction is more concentrated, and is discharged in successive quantities. That galvanism, if it be electrical, should be in such a state, seems to follow from the nature of the arrangement by which it is generated, which, consisting of a series of conductors, it is little accumulated, but must be conveyed as rapidly nearly as it is produced; while, from the nature of the electrical apparatus, this does not happen, the conducting power of the glass evolving it from friction being so inconsiderable. That galvanism does exist in this state of low intensity, appears from the spark from conductors of a galvanic battery being so small, and unable to overcome the resistance of the air, if the points of the conductors be at a very small distance. And this, as well as the rapidity of its evolution, are established with still more certainty by Van Marum's experiments, in which a charge of a battery of 137 square feet of coated surface, of as high intensity as could be communicated by a pile of 200 pairs, was made by a single contact, while, to give a charge of the same intensity from the most powerful electrical machine perhaps in Europe, required the momentary contact to be repeated six times. It is farther found, that when arrangements are formed which produce a stream of electricity in constant evolution, its effects are similar to those of galvanism. The experiment with this result was first made by Dr Wollaston. A silver wire, $\frac{1}{128}$ of an inch in diameter, was coated with sealing-wax, and cut through the middle, so as to expose a section of the wire: on immersing the

* Philosophical Journal, 4to, vol. iv, p. 243.

coated extremities of these two portions of wire at $\frac{1}{16}$ th of an inch distance from each other, in a solution of sulphate of copper, and placing them in the circuit of a common electrical machine in action, the wire on the negative side had a precipitate of copper formed on its surface; an effect the same with that which would have happened in the same solution at the negative wire of the galvanic battery. On reversing the direction of the current as to these wires, the copper was re-dissolved by the power of the wire, now rendered positive, while at the other, now negative, a similar precipitate of copper was formed. Other effects similar to those of galvanism were obtained *. Sir H. Davy employing a similar arrangement, found, that in placing the wires in connection with the electrical machine in action, in separate portions of sulphate of potash, the vessels being connected by moist asbestos, potash appeared in less than two hours around the negatively electrified point, and sulphuric acid around the positive point. On the other hand, from powerful galvanic batteries the spark can be taken at a considerable distance, the shock is communicated to the dry hand, and through a chain of persons; and very perfect insulation is required, circumstances all of which appear to prove the identity of the two powers.

Mr Donovan has more lately maintained the opinion † that electricity is not the cause of galvanic phenomena,—that though usually evolved in galvanic arrangements, it has only a very subordinate share in the effects. From an extensive series of experiments, he has established as general conclusions, that the sensations and muscular contractions produced by galvanism are not the consequences of electrical action, the two being in no proportion to each other,—that the heat and light, produced on completing the galvanic circuit, are equally independent of any elec-

* Philosophical Transactions for 1801, p. 429.

† Essay on Galvanism.

trical effect, and that the chemical changes produced by galvanism have in like manner no relation to the electric excitation, but are powerful when it is weak ; and, on the other hand, are not present when it exists in a high degree. He farther remarks, that in no case are any of these effects produced, but when chemical action is going forward in the component parts of a galvanic series ; and hence he has inferred, that they all arise from chemical action. The chemical attraction possessed by bodies is capable, he supposes, of being transferred from one body to another, in a manner somewhat similar to the transfer of some other attractive forces. Of two bodies between which such a transfer is made, one will lose its energy of action, the other will gain it. If two metals are in contact, he finds reason to infer from experiment, that one acquires an increased power of attraction to oxygen and acids, the other loses proportionally this power ; but it gains an attraction for hydrogen, for alkalis, earths and other metals. On this principle may obviously be explained the chemical decompositions produced by a galvanic series : the electricity produced, he considers as equally the effect of the transferred affinities in the metals composing the series, one kind of electricity being connected with certain affinities, the other with others : the exertion of affinity being usually accompanied, where it is intense, with the evolution of heat and light, the transfer of it may give rise to the same effects : and, lastly, sentient and irritable organs being sensible to the action of chemical stimuli, the sensations and contractions produced by galvanism may, he supposes, arise from transferred chemical action. These opinions, distinguished by their novelty, Mr Donovan supports with much ingenuity. Their probability, and the validity of the experimental results on which they rest, remain subjects of farther investigation.

On the principle that electricity and galvanism are the same power, there remains to be determined by what cause is it evolved in galvanic arrangements.

The facts with regard to the electric state of the voltaic series are, that its two extremities, while unconnected, are in the opposite states; the zinc positive; the copper negative; the two middle plates are neutral, and the liquid suffers little change. On connecting the extremities, the interposed liquid, or rather the saline compounds it contains, suffer decomposition; and the elements are attracted to the different plates; each zinc plate through the series is positive; hence the oxygen and acid of the liquor pass to the zinc surface, each copper-plate is negative, and the hydrogen and alkaline matter pass to it. The discharge at the two extremities proceeds; and this continues until the composition of the fluid is so far altered, that it exerts no farther chemical action. To account for this electric excitation under these conditions, two explanations have been given, one originally proposed by Volta, the other originating in the researches of Fabroni, modified by some of the British chemists.

Volta's hypothesis is deduced from the fact established by his own experiments, and also, though unknown to him, by the prior experiments of Bennet and Cavallo *, that "if two different metals, perfectly dry, insulated, and having only their natural quantity of electricity, be brought into contact, on removing them from that contact, they are in different electrical states; the one is positive, the other negative." In the example of the metals generally used in galvanic arrangements, the zinc is in the former state or *plus*, the copper is *minus*. The difference is not very considerable, but when accumulated in an electric condenser by repeated application of the plates, becomes sufficiently strong to cause the electrometer to diverge. Electricity, there-

* Nicholson's Journal, 8vo, vol. i.

fore, Volta concludes, is developed by the contact of different metals, independent of any foreign action on them ; or one metal, by its contact with another, forces part of its electricity into that other, and this inequality of distribution continues while they are in contact, and no conductor is applied to them. Different metals have different powers in this respect. Volta has placed them in the following order, from his experiments : silver, copper, iron, tin, lead, zinc, it being understood that the first causes electricity to move into the second, and those which follow it, the second into the third, &c. Charcoal, plumbago and black oxide of manganese, have a similar power. This property in bodies is named their electro-motive power.

If a series of metallic plates were constructed, without any intermediate substance, what would be the result of this action ? Copper commencing the series, and in contact with a plate of zinc above it, would yield to the zinc part of its electricity, which would become positively charged. But if another plate of copper were placed on the other side of the zinc, this action would be interrupted, the zinc being in contact at each of its surfaces with the two plates of copper, two equal forces would act in opposite directions, and counterbalance each other. Hence the difference in the electrical state would not be greater in the whole series than in a single pair of the plates, and would even amount to nothing if it began and ended with the same metal. But if a piece of moist card be placed between the plates, as in the above example between the zinc plate and the second copper plate, the effect of the latter on the former is interrupted ; the liquid in the card having comparatively little of this electro-motive power, does not interrupt the motion, while it conveys the positive electricity from the zinc to the next copper plate : accordingly, on this addition of the moistened card, Volta found that signs of electricity are manifested in the series : And it was on this reasoning that he was led to the con-

struction of the arrangement which constituted his splendid discovery.

On these principles, then, may be explained the evolution and motion of electricity in the voltaic series. Suppose the pile to commence with a plate of copper on an insulated base, and that over this is placed a plate of zinc, by the contact the copper loses a portion of its electricity, which the zinc acquires; the former becomes negative, the latter proportionally positive; if a piece of moistened paste-board be placed over the zinc, it does not counteract, or does so in so slight a degree as to admit of being neglected, the action between the pair of plates, but operating as a conductor, a piece of copper placed above it acquires the same electric state as the zinc below. The pile being supposed insulated, this can be done only at the expence of the undermost copper plate, and hence it loses more of its electricity, or becomes more highly negative. On placing over the second copper plate a second plate of zinc, it must, from their mutual action, acquire more electricity than the copper over which it is placed, which must still be at the expence of the pieces beneath; each of these will therefore suffer a proportional diminution; the first, or that which commenced the pile, will become more highly negative than before; the second and third pieces, which were positively charged, will have that charge diminished, and approach nearer to their natural state; the second one more so than the third; while the upper piece, which is the second plate of zinc, will be more highly positive. In this manner, the quantity of electricity in the upper plate will increase in arithmetical progression, while it will be proportionally diminished at the base, and the two extremities will be in the opposite electrical states, the difference being greater according to the number of plates; and as many degrees as the plate at the head of the column is positive, so many will that at the bottom be negative, while in the middle of the column there will be two plates in

their natural state, which Volta accordingly found to be the case. When a communication is made by a conductor between the two extremities, a current of electricity is established ; or if a communication be established between the earth and the base of the pile, and a communication of the other extremity with conductors, the metal, which yields electricity to the other, receives it from the earth, continues still to give it to the other, from which it is carried forward by the contiguous fluid or humid substance, and thus a constant current, increasing as it proceeds, is established.

The powers of different liquids in exciting electricity, Volta ascribes to their different conducting powers, modified as they have less of the electro-motive quality ; those which are the best conductors being superior in exciting effect ; this superior conducting power being probably necessary from the low state of electrical intensity in the apparatus, to transmit the electrical state from the one pair of plates to the other. Saline liquors, which are superior to water in exciting power, are better conductors of electricity than water, as was established prior to Volta's researches, by those of Priestley and Morgan ; and Volta farther found what is conformable to the mode of operation he supposes, that although the effects are more considerable when they are employed, the tension indicated by the electrometer does not equally increase, but appears even to be the same, at least in comparing water with a solution of sea-salt. The different powers of the different metals, he supposes owing to the degrees in which they possess the electro-moving power, zinc taking electricity from every other, and gold yielding it to the rest. The action which puts in motion the electric energy, though greatest between the metals, he finds exists in a less degree in other substances, as in charcoal, metallic oxides, and a number of liquids : between some liquids and me-

tals it is such as to allow of a galvanic arrangement being formed with a single metal: in this way is explained the construction of such an arrangement, from a metal with its different sides in contact with diluted nitric acid and a solution of sulphuret of potash. And if there were solid substances conductors of electricity without having the electro-motive power, a pile might even be constructed by their medium, without the intervention of fluid. If a greater difference, for example, existed between three metals in the electro-motive quality than does exist, an electric column might be formed entirely metallic, and permanent in its operation *.

The hypothesis opposed to Volta's, is that which supposes the electricity in a galvanic series to be evolved in consequence of the chemical action of the substances composing it. It was suggested by the researches of Fabroni, with regard to the mutual action of metals. He had observed, that metals when pure preserve their lustre for a long time, but that their alloys are quickly tarnished, and oxidated by exposure to the air; that the contact of two metals hastens the oxidation of each; and hence, as he found, that if pure metals be put in separate vessels of water, they are not altered; but if two of them be immersed in water in contact, the more oxidable one is soon loaded with oxide. The signs of electricity observed when two metals are separated from contact, were considered as the consequence of this chemical action rather than the cause; all the other phenomena, even the sensations which the metals excite, Fabroni regarded as the immediate effects of the chemical action, and not the effects of the electrici-

* Report to the National Institute, translated in the *Philosophical Magazine*, vol. xi, p. 301. Letter of Volta, translated in *Nicholson's Journal*, 8vo, vol. i, p. 135., and *Memoir by Volta*, *Annales de Chimie*, t. xl, p. 225.

ty which that action evolves *. This correction, however, was soon made by the British chemists; the evolution of electricity in the galvanic apparatus was ascribed to the chemical action in the parts composing it; and on this principle a theory was presented under different modifications, which has received more precision in the progress of the investigation. The following is the manner in which it may be understood.

In consequence of the chemical action of the liquid in a galvanic series on the metal which suffers the greatest change, the relation of that metal to the electrical state is so altered, that electricity flows to the surface acted on. This determines the motion of the electrical power to that surface from the rest of the mass of metal. Hence, supposing a plate of zinc to consist of a number of layers, the external layer acted on by the liquid giving out its electricity, and the other layers yielding a corresponding portion in their turn, the electricity in the entire plate is put in motion, and the direction is from the opposite side of the plate towards that which is suffering the chemical change. The latter becomes positive, the former negative; and this last state is of course communicated to the copper plate which is in contact with that surface of the zinc. Were the next plate in the series to be zinc, the same chemical action would be exerted by the liquid at its surface. The same evolution of electricity would in consequence be produced, and this would be in a direction contrary to that from the other. But the next metallic surface being copper, and this metal not being much acted on by the liquid, this is prevented; the copper receives, by the medium of the interposed liquid, the electrical state of the preceding pair of plates, which it communicates to the zinc connected with it. At the surface of the zinc plate exposed to the action of the liquid, the same action goes on as in the

* Nicholson's Journal, 4to, vol. iv, p. 120.

former: a fresh portion of electricity is evolved in consequence of it, and this must be supplied from the plates behind: this is repeated at each pair of plates in the series: the copper plate therefore at the commencement is becoming more highly negative, and the zinc plate which terminates it is proportionally positive. Thus, according to this hypothesis, the evolution of electricity depends entirely on the chemical action of the liquid on the metal which is most susceptible of that action, and the other metal is useful only in that it is not chemically acted on to any great extent, and does not therefore, by any contrary evolution of electricity, counteract the effect produced at the surface of the metal suffering the chemical change.

In comparing the merits of these hypotheses, difficulties are found to be attached to each, as well as facts in their support.

Volta's doctrine seems to afford a satisfactory explanation of the leading phenomenon,—the excitation of electricity in the series, if the principle be admitted, that metals by contact alter the electric equilibrium, so as to pass into the different states, while liquids have little of this electro-motive power. But the fact with regard to this is called in question, and must be admitted to be doubtful. The signs of electricity are manifested only when the separation of the metals has been effected; and there is no proof, that while they are in contact, they are in different electrical states. The explanation, too, which Volta gives of the effect of the interposed liquid, that it depends on its acting as a conductor between the pair of plates, is scarcely satisfactory, particularly when the very great differences of exciting effect in different liquids are compared. It is true that the difference is not supposed in the theory to be merely according to the difference in conducting power, but to this modified by the electro-motive quality which these liquids exert to a certain extent, and which so far counteracts the accumulation from the action of the me-

tals. But even with this modification the application to the actual results is by no means obvious, or sufficiently established. On the other hand, the connection in the exciting effect of the liquid with its chemical energy, and the degree of change it produces, seems so general, that it can scarcely be supposed but that an important share of it depends on this action. The facts proving this are numerous, and were established by different experimentalists, Haldane, Davy, Pepys, Biot, Van Marum, and others *. Pure water, for example, has scarcely any exciting effect, while, if it hold dissolved atmospheric air, oxygen gas, nitric oxide, or, still more, if a small portion of an acid be added to it, it acts with increased energy. The action of the pile has even been found to be influenced by the chemical energy of the surrounding elastic medium: if the cards are moistened with pure water, it ceases when it is placed in *vacuo*, in nitrogen, or hydrogen gas; it is renewed, and continues for a limited time in atmospheric air; it is still more energetic in oxygen gas, and the oxygen is consumed. Or if nitric acid, or even a saline solution, be added to the water moistening the cards, the action proceeds *in vacuo*. The connection between the evolution of voltaic electricity and the chemical action of the substances from which it is evolved, is not less proved by the ceasing of the excitation in the battery when the chemical power of the liquid is exhausted by its action on the metals, though it can scarcely be supposed that this shall diminish so much its conducting quality, or exalt its electromotive power as to account for the cessation of effect. Lastly, the power of the metals in affording galvanism seems to be in some measure connected with their susceptibility of being chemically acted on; zinc, for example, which is the one most oxidable, forming the most power-

* Nicholson's Journal, 4to, vol. iii. & iv. Annales de Chimie, t. xl.

ful arrangement, and always suffering oxidation when it affords galvanic effects.

These facts, however, perhaps only justify the conclusion, that chemical action has some share in modifying the production of galvanism, not that it is the sole cause of its evolution; and there are others of an opposite kind, or which prove that the powers of different liquids in the galvanic battery are not proportional to their chemical agency. Thus, next to acids, the solutions of pure potash, of muriate of soda, and muriate of ammonia, are most effectual in promoting it; yet they do not exert any great chemical energy. If we compare the action they do exert, with that of other substances which likewise act on metals but which generate less galvanism, or with the rapid action of acids, and compare their exciting galvanic powers, it will appear that these are in no proportion, but that the exciting powers of the solutions of these salts are greater than what such a theory would suggest. With regard to potash, for example, it exerts so little chemical action on the metals, that according to Van Marum their polish is not even impaired *. The same conclusion will follow from the comparative action of the different acids. Sulphuric acid, diluted, has less power than muriatic or nitric acid in exciting galvanism; yet its chemical action on the metals in a galvanic arrangement is as energetic. This fact of the power of the interposed fluid in exciting galvanism, being not proportional to its chemical energy so well displayed in the example of a solution of sea-salt, seems conclusive against the hypothesis, that chemical action is the primary cause of galvanic excitation. It is also to be considered, that metals, after separation, exhibit electrical phenomena; and whether the change be supposed to arise from their contact or from their separation, it is at least independent of chemical action. Even in the subversion of

* Nicholson's Journal, 8vo, vol. i, p. 180.

the electric equilibrium from this contact or separation of metals, there appears to be some connection between the electro-motive quality and their chemical energies, that metal of the two always becoming positive which has the strongest attraction to oxygen, though there is certainly no chemical action exerted ; —and hence the relation of powerful chemical agents, of acids for example, to the excitation in the voltaic series, may not depend on the chemical changes which they actually produce.

The doctrine too, that the evolution of electricity in voltaic arrangements depends entirely on chemical action, is purely hypothetical. Nor is the explanation which it gives of the accumulation of power, and of the difference of electric states at the two extremities of the series, very satisfactory.

Were the principle of Volta's theory, that metals, by contact, break the electric equilibrium, established, these considerations would probably be sufficient to lead to its adoption in preference to the other, since, with the admission of this, it appears to follow, that in an arrangement such as that of the galvanic pile, the electricity must increase through the series ; and if chemical action has any influence, it is probably only a subordinate one in modifying the effect. The principle, however, it has been remarked, is doubtful, though not disproved. Yet, even admitting it, the difficulty remains of explaining with any precision in what manner the interposed liquid by its chemical action modifies the mutual electric action of the metals, so as to contribute to the more active production of electricity. Of various hypotheses proposed to illustrate this, the most probable perhaps is that suggested by Sir H. Davy. He considers the chemical action of the fluid as contributing to the effect by its elements being evolved in different electrical states, communicating these to the plates, and by the renewal of electricity giving permanence to the excitation. Each plate of the one metal in the series is positive, each plate of the other metal is negative,

and the plates have by induction these electric states exalted, so that with an increase of number there is an accumulation of power. When the extremities are unconnected, and the battery is insulated, it remains in this state, and no chemical changes are observed in the interposed fluid. When the circuit is completed by communication between the extremities, the decomposition of the fluid takes place, and its elements acquire different electrical states; those which are negative, oxygen and acids, for example, pass therefore to the positive metallic plates; those which are positive, such as hydrogen and alkalies, pass to the negative metallic plates; and there is thus a renewal of power to supply the discharge while the chemical action proceeds. It is difficult to conceive, however, of the electric states being established by induction, and especially of their being augmented by it, in a conducting medium so perfect as that of the fluids which are most powerful in exciting galvanism; nor is it very apparent how the elements of the fluid should continue to pass into the electric states, so as to afford so great an evolution of power. And the subject must still be considered as involved in that obscurity which precludes a satisfactory theory.

MISCELLANEOUS TABLES.

THE greater number of the results, which it is of advantage to represent in tables, have been inserted under that form at the close of the preceding chapters on Attraction and on Caloric. Some others connected with the properties of particular substances will be best placed under the history of these substances. There are, however, a few miscellaneous tables, not easily referred to any particular subject, but chiefly connected with the general doctrines or the operations of chemistry, which have been illustrated in this volume. These I add in a small Appendix.

The first are tables of the Specific Gravities of the Gases. It has been observed, (p. 296,) that in experiments on aërial substances, their quantities are usually found by volume, and from this are referred to weight, according to their specific gravity. So many chemical compounds being gaseous, or composed of gaseous elements, it becomes a point of great importance, both in reference to the general theory of chemical combination, and to the details of chemistry, that the specific gravities of the gases should be determined with the greatest precision; and this too more especially, as a slight deviation from accuracy in the estimate leads to errors of considerable moment. The subject has, therefore, occupied much the attention of chemists, and the results have been repeatedly corrected. I insert the two latest tables that have been constructed. The first is one by Dr Thomson, (*Annals of Philosophy*, vol. vii, p. 343.) ; the second is by Gay-Lussac, (*Annales de Chimie et Physique*, t. i, p. 218. translated *Annals of Philosophy*, vol. ix, p. 16.)

Dr Prout had suggested a relation between the specific gravities of the gases and their combining quantities, or the weight of their atoms, the specific gravity being found, he affirmed, by multiplying half the specific gravity of oxygen by the weight of the atom of the gas with respect to oxygen. He calculated also the specific gravities of oxygen and nitrogen gases on the assumption, that atmospheric air is a chemical compound of four volumes of nitrogen and one volume of oxygen: And although this proposition is doubtful, the numbers thus assigned are very nearly the mean of those which can be regarded as accurate. And by calculating the specific gravity of hydrogen gas from the specific gravity of a denser compound in which it exists in known proportion, ammonia, and the weight of which is more easily determined, he reduces it, perhaps with more accuracy, a little below that which had been usually found from experiment. Dr Thomson has adopted these views, and his table is conformable to them. Gay-Lussac's rests on experimental results, or on calculation from gaseous compounds in which the elements exist, and these are given in separate columns. The authorities are annexed to the table, and some observations with regard to them are stated in his paper. Some discussions connected with these determinations will also be found in the papers of Dr Prout and Dr Thomson, *Annals of Philosophy*, vol. vi, p. 321, vol. vii, p. 343, vol. i, p. 177.

Dr Thomson adds, that in relation to the correspondence between the specific gravities, and the weights of their atoms, the gases may be reduced under three classes; in the first, the specific gravity, and the weight of the atom are represented by the same number; in the second, the weight of the atom is double that of the specific gravity; and in the third, the weight of an atom is equal to four times the specific gravity—reducing the specific gravities to the same standard as the weights of the atoms. Assuming oxygen as the standard, there are two gases, oxygen and olefiant gas, belonging to the first class; five belong to the third, hydriodic acid, muriatic acid, nitrous gas, hydro-cyanic acid, and ammonia; and all the others in the table belong to the second.

TABLE I.

GASES.	Spec. Gravity.	Weight of 100 cub. inch in grs.
Air,	1.000	30.5
Hydriodic acid gas,	4.429	135.084
Phosgene gas,	5.459	104.891
Chlorine gas,	2.500	76.250
Euchlorine,	2.440	74.420
Sulphurous acid,	2.222	67.771
Cyanogen,	1.801	54.933
Nitrous oxide,	1.5278	46.598
Carbonic acid,	1.527	46.373
Muriatic acid,	1.284	39.162
Sulphuretted hydrogen,	1.180	35.890
Sulphur vapour,	1.111	33.888
Oxygen,	1.111	33.888
Nitrous gas,	1.0416	31.769
Olefiant gas,	0.974	29.72
Azote,	0.9722	29.652
Carbonic oxide,	0.972	29.652
Hydro-cyanic acid vapour,	0.937	28.58
Steam,	0.625	18.062
Ammonia,	0.590	18.000
Carburetted hydrogen,	0.555	16.99
Carbon vapour,	0.416	12.688
Hydrogen,	0.0694	2.117

TABLE II.—Gaseous Bodies.	Sp. Gr. by exper.	Ditto calcu- lated.	Experimenters.
Air	1.0000		
Vapour of iodine		8.6195	Gay-Lussac. Ann. de Chim. xci. 17.
Vapour of hydriodic ether	5.4749		Gay-Lussac.
Vapour of oil of turpentine	5.0130		Gay-Lussac.
Hydriodic acid gas	4.4430	4.4288	Gay-Lussac. Ann. de Chim. xci. 16.
Fluo-silicic acid gas	3.5735		John Davy. Phil. Trans. 1812, p. 354.
Phosgene gas		3.3894	Id. Ib. p. 150.
Nitrous acid gas		3.1764	Gay-Lussac.
Vapour of sulphuret of car- bon	2.6447		Gay-Lussac.
Vapour of sulphuric ether	2.5860		Gay-Lussac.
Chlorine	2.4700	2.4216	Gay-Lussac and Thenard.
Euchlorine		2.3144	Gay-Lussac.
Fluo-boric gas	2.5709		John Davy. Phil. Trans. 1812, p. 366.
Vapour of muriatic ether ...	2.219		Thenard. Mem. d'Arcueil, i. 121.
Sulphurous acid gas	2.1950	2.2072	Davy.
Chloro-cyanic vapour		2.1113	Gay-Lussac. Ann. de Chim. xcv. 110.
Cyanogen	1.8064	1.8011	Id. Ib. p. 177.
Vapour of absolute alcohol	1.6133	1.60 0	Gay-Lussac.
Nitrous oxide	1.5204	1.5209	Colin.
Carbonic acid	1.5196		Biot and Arago. Mem. de l'Institut. 1806, p. 320.
Muriatic acid	1.2474	1.2505	Id. Ib. p. 320.
Sulphuretted hydrogen	1.1912	1.1768	Thenard and Gay-Lussac. Recherch. i. 191.
Oxygen	1.1036		Biot and Arago. Mem. de l'Institut. 1806, p. 320.
Nitrous gas	1.0388	1.0364	Berard.
Olefiant gas	0.9784		Th. de Saussure. Ann. de Chim. lxxxix. 283.
Azote	0.9691		Arago and Biot. Mem. de l'Institut. 1806, p. 320.
Oxide of carbon	0.9569	0.9678	Cruikshank.
Hydro cyanic vapour	0.9476	0.9360	Gay-Lussac. Ann. de Chim. xcv. 150.
Phosphuretted hydrogen ...	0.870		Davy.
Steam	0.6235	0.6250	Gay-Lussac.
Ammonia	0.5967	0.594	Biot and Arago. Mem. de l'Institut. 1806, p. 320.
Carburetted hydrogen	0.5550	0.5624	Thomson.
Arseniated hydrogen	0.5290		Trommsdorf.
Hydrogen ...	0.0732		Arago and Biot. Mem. de l'Institut. 1806, p. 320.

Another table of the specific gravities of the gases has been given by Professor Meinecke, in which they are referred to air, to oxygen, and to hydrogen, as standards, and which is convenient, therefore, as exhibiting these relations. The specific gravities of hydrogen and oxygen are somewhat different from those usually assigned, hydrogen being only one-sixteenth of oxygen. This is the same which had been assigned by Dr Prout, and probably has been adopted by Meinecke from the same considerations. The table is from the 10th volume of the *Annals of Philosophy*.

	Air being 1.000.	Hydrogen being 1.000.	Oxygen being 1.000,
Hydrogen,	0.0694	1	0.0625
Carburetted hydrogen,	0.5555	8	0.5000
Ammonia,	0.5901	$8\frac{1}{2}$	0.5312
Steam,	0.6250	9	0.5625
Hydrocyanic acid vapour, .	0.9374	$13\frac{1}{2}$	0.8437
Carbonic oxide,	0.9722	14	0.8750
Olefiant gas,	0.9722	14	0.8750
Azote,	0.9722	14	0.8750
Air,	1.000	$14\frac{2}{3}$	0.900
Deutoxide of azote,	1.041	15	0.937
Oxygen,	1.111	16	1.000
Sulphuretted hydrogen, ...	1.150	17	1.062
Muriatic acid,	1.274	$18\frac{1}{2}$	1.156
Carbonic acid,	1.527	22	1.375
Protoxide of azote,	1.527	22	1.375
Vapour of alcohol,	1.597	23	1.437
Cyanogen,	1.806	26	1.625
Chlorocyanic acid vapour, .	2.153	31	1.937
Sulphurous acid,	2.222	32	2.000
Chlorine,	2.500	36	2.250
Vapour of ether,	2.569	37	2.312
Nitrous acid,	2.638	38	2.375
Sulphuret of carbon,	2.638	38	2.375
Phosgene gas,	3.473	50	3.125

TABLE FOR CONVERTING ENGLISH OUNCE MEASURES INTO
ENGLISH CUBIC INCHES.

THE ounce measure has been often employed by chemists in expressing the volumes of elastic fluids. It is also often used in the graduation of our measures, and hence the convenience of a table expressing the relations of measures by it, to those by the more general standard of the cubic inch.

Ounce measures.	English cubical inches.	Ounce measures.	English cubical inches.
1	1.898	20	37.960
2	3.796	30	56.940
3	5.694	40	75.920
4	7.592	50	94.900
5	9.490	60	113.880
6	11.388	70	132.860
7	13.286	80	151.840
8	15.184	90	170.820
9	17.082	100	189.800
10	18.980	1000	1898.000

TABLE OF CORRESPONDENCE BETWEEN ENGLISH CUBIC INCHES OF
WATER AT 60° OF TEMPERATURE. AND ENGLISH TROY GRAINS.

Cubic inches of water.	Troy grs.	Oz.	Dr	Grs.
1	252.506	0	4	12.506
2	505.012	1	0	25.012
3	757.518	1	4	57.518
4	1010.024	2	0	50.024
5	1262.530	2	5	2.530
6	1515.036	5	1	15.036
7	1767.542	5	5	27.542
8	2010.048	4	1	40.048
9	2272.554	4	5	52.554
1728 (1 cub. foot)	—	909	0	10.568

TABLE OF FRENCH AND ENGLISH CUBIC INCHES.

Cubic inches.			Cubic inches.		
<i>French.</i>	=	<i>English.</i>	<i>English.</i>	=	<i>French.</i>
1		1.2156	1		0.8259
2		2.4272	2		1.6479
3		3.6408	3		2.4719
4		4.8544	4		3.2958
5		6.0681	5		4.1198
6		7.2817	6		4.9458
7		8.4953	7		5.7677
8		9.7089	8		6.5917
9		10.9225	9		7.4157
10		12.136	10		8.239
20		24.272	20		16.479
30		36.408	30		24.719
40		48.544	40		32.958
50		60.68	50		41.198
60		72.817	60		49.458
70		84.953	70		57.677
80		97.089	80		65.917
90		109.225	90		74.157
100		121.36	100		82.39
200		242.72	200		164.79
300		364.08	300		247.19
400		485.44	400		329.58
500		606.81	500		411.98
600		728.17	600		494.58
700		849.53	700		576.77
800		970.89	800		659.17
900		1092.25	900		741.57
1000		1213.6	1000		823.9
2000		2427.2	2000		1647.9
3000		3640.8	3000		2471.9
4000		4854.4	4000		3295.8
5000		6068.1	5000		4119.8
6000		7281.7	6000		4945.8
7000		8495.3	7000		5767.7
8000		9708.9	8000		6591.7
9000		10922.5	9000		7415.7
10,000		12136.0	10,000		8239.0

TABLE OF FRENCH AND ENGLISH GRAINS.

Grains.		Grains.	
<i>French</i>	<i>English</i>	<i>English</i>	<i>French</i>
1	0.8203	1	1.2189
2	1.6407	2	2.4378
3	2.4611	3	3.6568
4	3.2815	4	4.8757
5	4.1019	5	6.0947
6	4.9223	6	7.3136
7	5.7427	7	8.5325
8	6.5631	8	9.7515
9	7.3835	9	10.9704
10	8.203	10	12.189
20	16.407	20	24.378
30	24.611	30	36.568
40	32.815	40	48.757
50	41.019	50	60.947
60	49.223	60	73.136
70	57.427	70	85.325
80	65.631	80	97.515
90	73.835	90	109.704
100	82.03	100	121.89
200	164.07	200	243.78
300	246.11	300	365.68
400	328.15	400	487.57
500	410.19	500	609.47
600	492.23	600	731.36
700	574.27	700	853.25
800	656.31	800	975.15
900	738.35	900	1097.04
1000	820.5	1000	1218.9
2000	1640.7	2000	2437.8
3000	2461.1	3000	3656.8
4000	3281.5	4000	4875.7
5000	4101.9	5000	6094.7
6000	4922.5	6000	7313.6
7000	5742.7	7000	8532.5
8000	6563.1	8000	9751.5
9000	7383.5	9000	10970.4
10,000	8203.0	10,000	12189.0

TABLE OF FRENCH MEASURES AND WEIGHTS REDUCED TO THE
ENGLISH STANDARD, AT THE SAME TEMPERATURE.

Measures of Length.

E. Inches.

Millimetre.....	.03937
Centimetre.....	.39371
Decimetre	3.93710
Metre..... (3.281 feet).....	39.37100
Decametre	393.71000
Hecatometre.....	3937.10000
Chiliometre.....	39371.00000
Myriometre	393710.00000

Measures of Capacity.

E. Cubic Inches.

Millilitre06105
Centilitre61028
Decilitre	6.10280
Litre (a cubic decimetre).....	61.02800
Decalitre.....	610.28000
Hecatolitre.....	6102.80000
Chiliolitre... ..	61028.00000
Myriolitre.....	610280.0000

Weights.

E. Grains.

Milligramme0154
Centigramme1544
Decigramme	1.5444
Gramme (weight of a cubic centimetre of water,)	15.4440
Decagramme.....	154.4402
Hecatogramme	1544.4023
Chiliogramme	15444.0234
Myriogramme	154440.2344

END OF VOLUME FIRST.



Fig. 13.

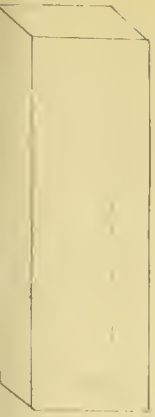


Fig. 14.

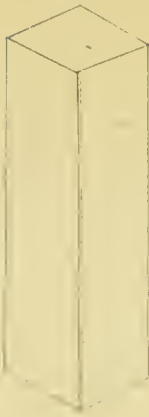


Fig. 15.

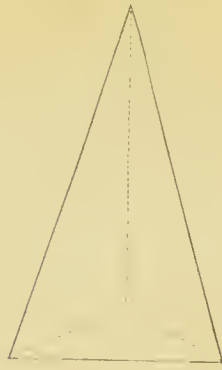


Fig. 16.

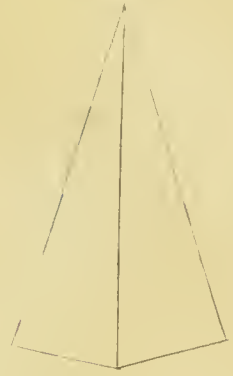


Fig. 17.



Fig. 18.



Fig. 19.



Fig. 20.



Fig. 21.



Fig. 22.



Fig. 23.

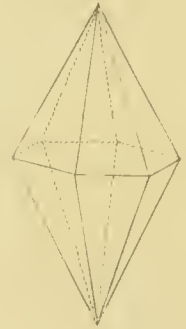


Fig. 24.



Fig. 25.

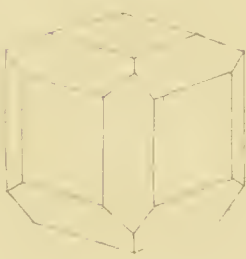


Fig. 26.



Fig. 27.



Fig. 28.

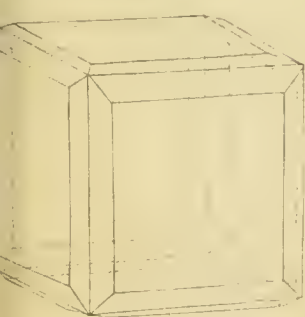


Fig. 29.

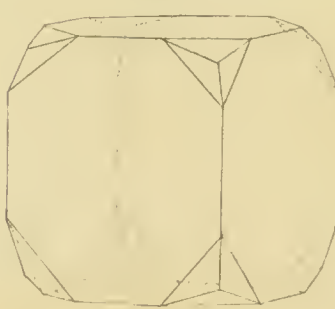


Fig. 30.

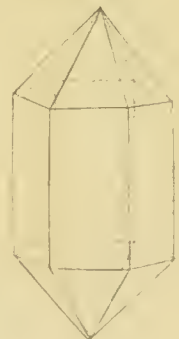


Fig. 31.

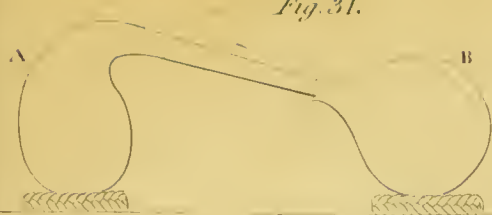


Fig. 32.

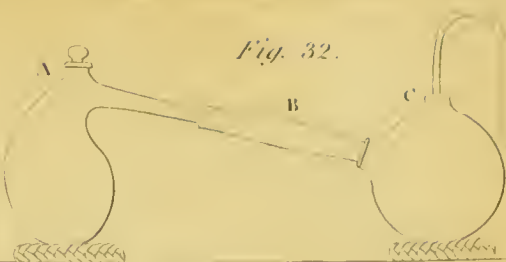


Fig. 33.

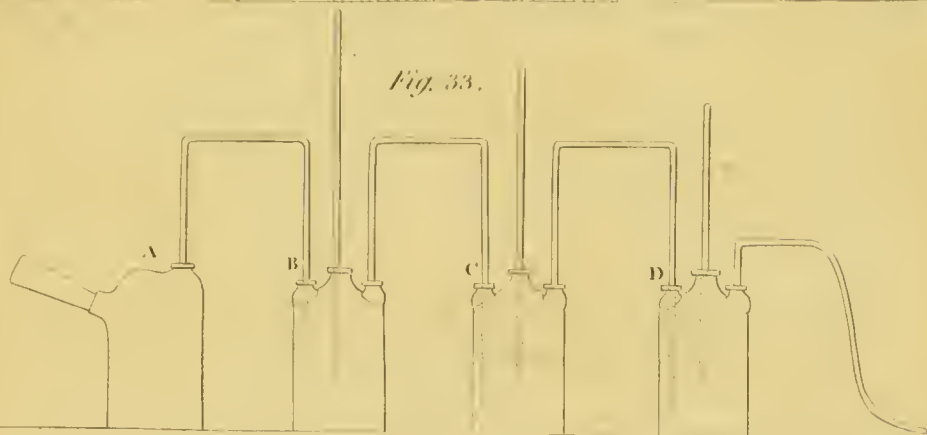


Fig. 34.

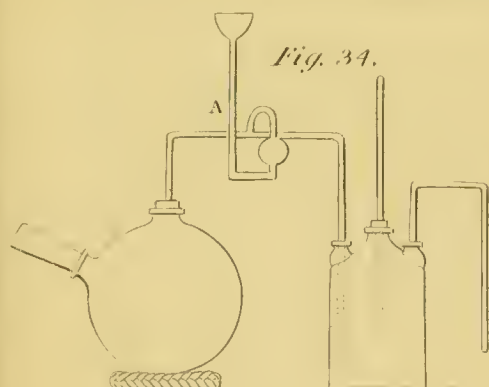


Fig. 35.

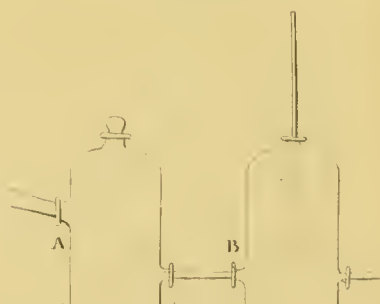


Fig. 36.

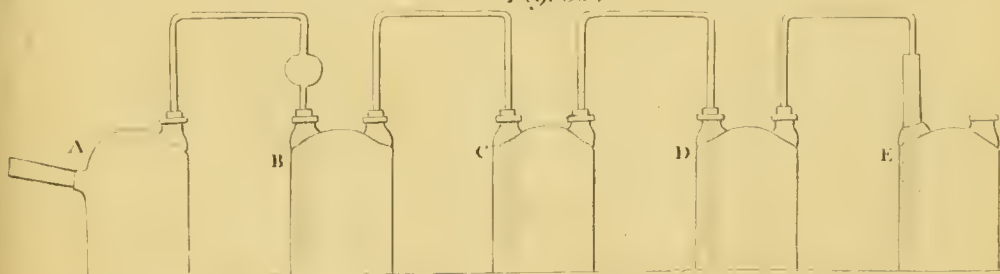


Fig. 37.

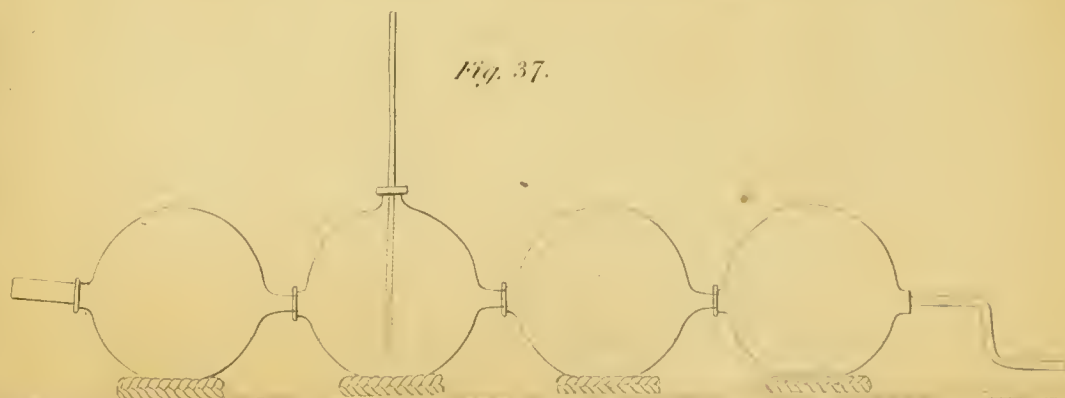


PLATE IV.

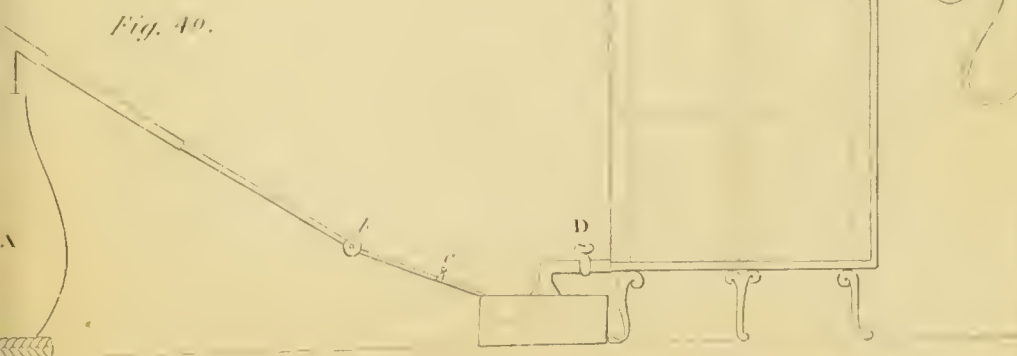
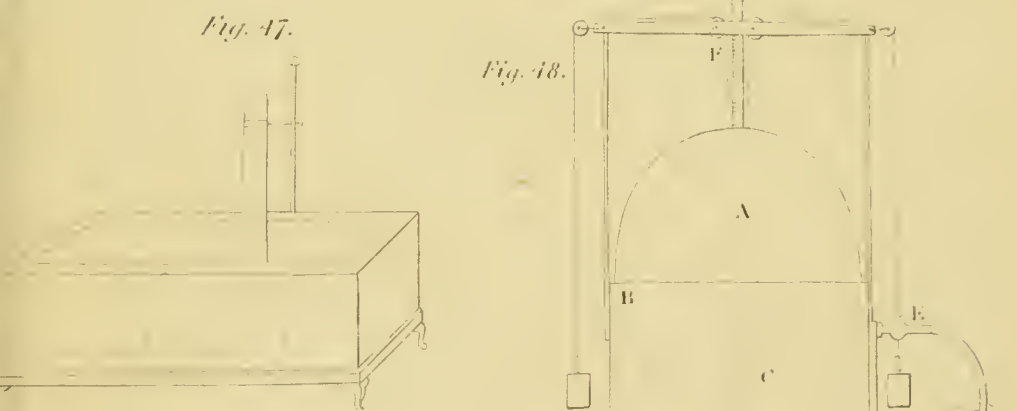
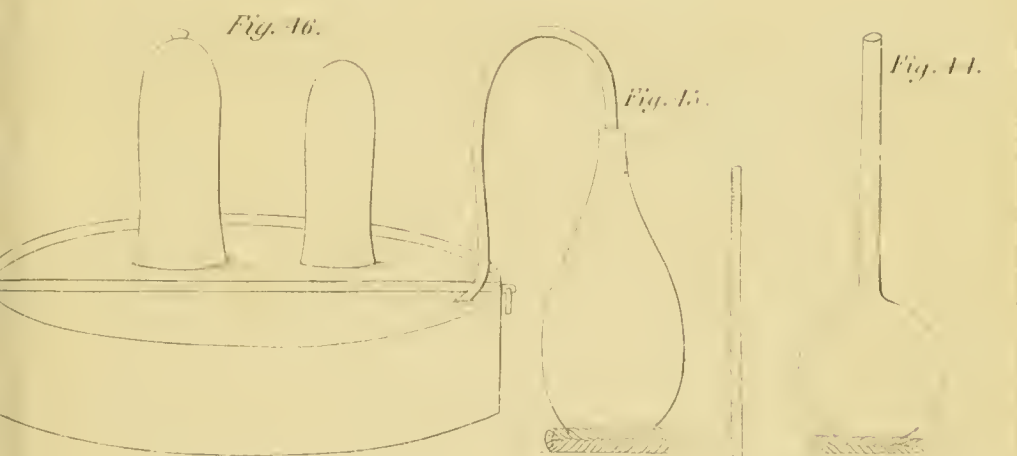
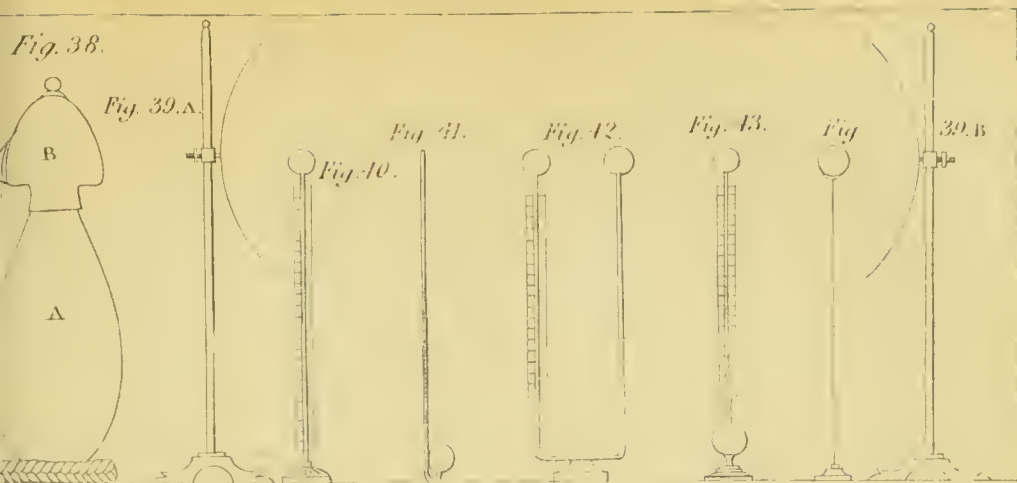


Fig. 50.



Fig. 51.



Fig. 52. Fig. 53.

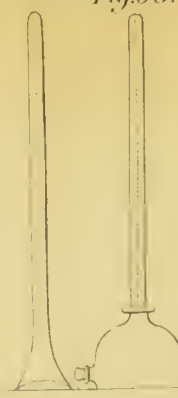


Fig. 54.

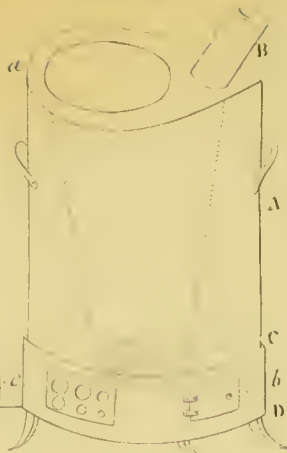


Fig. 55.

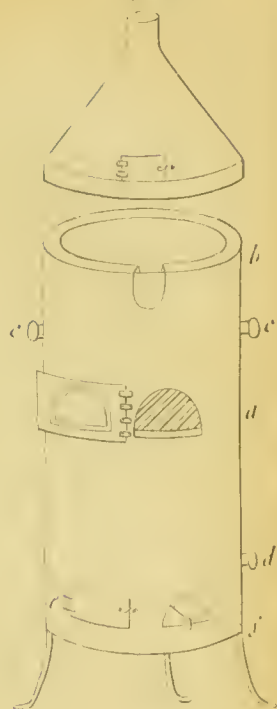


Fig. 57.

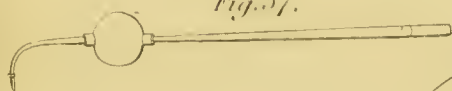


Fig. 56.



Fig. 58.

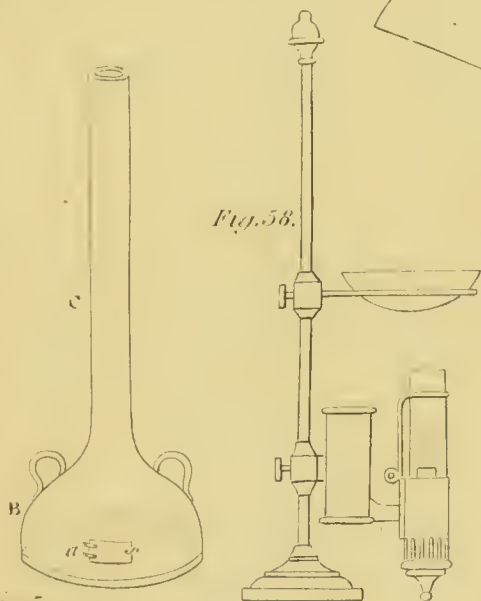


Fig. 63.

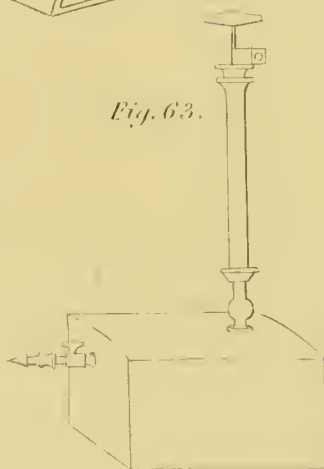


Fig. 62.

Fig. 59.

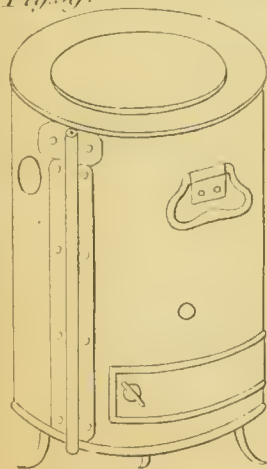


Fig. 60.



Fig. 61.

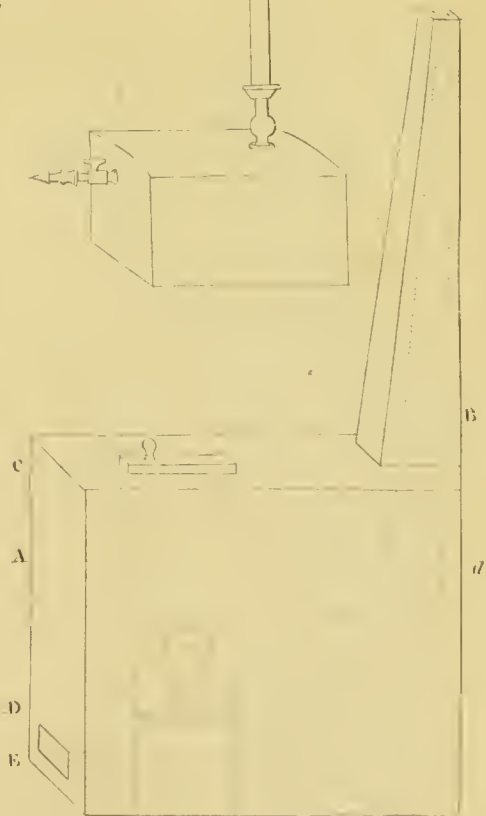




Fig. 64.

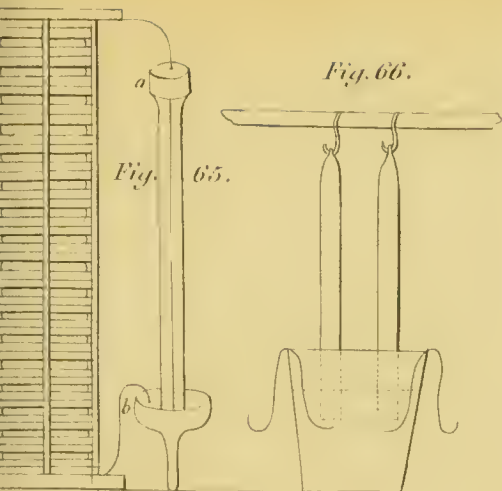


Fig. 66.

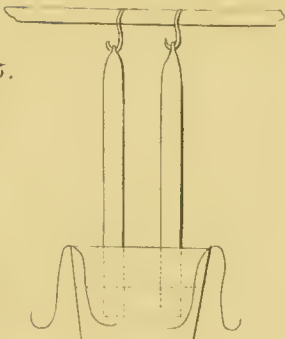


Fig. 65.

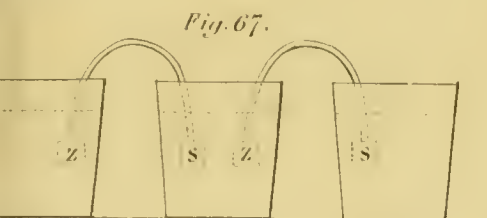


Fig. 67.

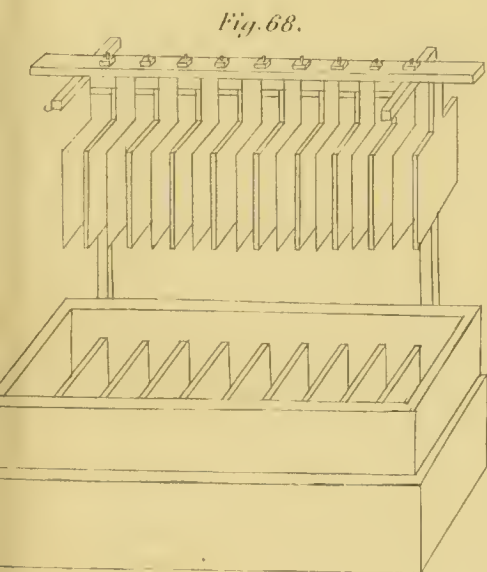


Fig. 68.

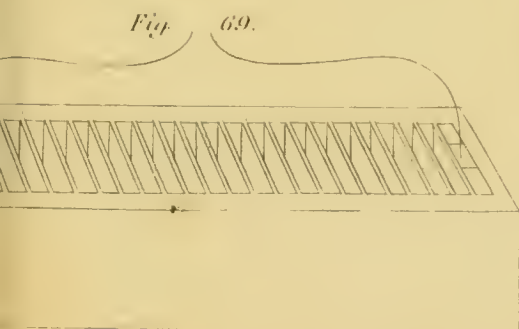


Fig. 69.

		Abbreviations
Oxygen	10	d . dry
Water	11	c . crystallized
	12	Ox. Oxid
		Carb. Carbonate
10 Hydrogen	13	M. Muriate
	14	N. Nitrate
	15	S. Sulphate
	16	W. Water
Phosphorus	17	Azote
	18	
2 Oxygen	19	
	20	Sulphur
	22	Ammonia
		2 Water
	24	Magnesia
Calcium	26	
	28	Carbonic acid
Sodium	30	
3 Oxygen	32	
	34	Muriatic acid d
Iron	36	Lime
Phosphoric acid	38	Nitrous gas
	40	Soda
Copper	42	Zinc
	44	Ox. Iron
Chlorine	46	Sub. Carb. Ammonia
Muriatic gas	48	Potassium
Oxalic acid	50	Red Ox. Iron
Sulphuric acid	52	Ox. Zinc
5 Oxygen	54	
Ox. Copper	56	
2 Carbonic acid	58	5 Water
	60	Potash
6 Oxygen	62	
Oil of Vitriol	64	Carb. Lime
S.G. 1.85	66	Sub. Carb. Soda d
d Nitric acid	68	M. Ammonia
Strontia	70	M. Lime d
	72	M. Soda
10 Carbon	74	S. Magnesia d
Bi Carb. Ammonia	76	7 Water
	78	
Sub. Carb. Potash	80	S. Lime d
Liquid Nitric acid	82	S. Soda d
S.G. 1.50	84	M. Potash
Barytes	86	
	88	
N. Lime	90	Bi Carb. Soda
N. Soda	92	Schulte 2 W c.
S. Potash	94	10 Water
	96	
S. Strontia	98	Carb. Barytes
Bi Carb. Potash	100	N. Potash
Mercury	102	M. Barytes d
Lead	104	Red Acid q
Silver	106	
Litharge	108	S. Barytes
Ox. Silver	110	S. Magnesia c. 7 W
Bin Oxal Potash	112	
60 Oxy. M Potash	114	N. Barytes
c. 5 W S. Copper	116	Carb. Lead
	118	S. Iron c. 7 W
Corros. Sublimate	120	M. Lead
Phosph. Lead	122	S. Zinc c. 7 W
Mar. Silver	124	Oxalate Lead
S. Lead	126	



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$\frac{23}{4}$ 79 25

